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Since most large molecules and colloidal particles carry a charge, electrophoresis is obviously a convenient method of separation. However, the disadvantage is that, when the potential gradient is merely applied across a buffered solution of the material to be separated, re-mixing may occur owing to convection currents, and complete resolution of the fractions is not possible.

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ELECTROPHORETIC ANALYSIS OF SERUM PROTEINS IN CHRONIC RHEUMATIC DISEASES

The analysis of serum protein for purposes of diagnosis has been greatly advanced by paper electrophoresis. Kunkel and Tiselius (*J. Gen. Physiol.*, **35**: 89. 1951-2) have described a procedure which is 'extremely simple and surprisingly accurate', but lay great stress upon the importance of using the right filter paper. The reason for this is that, though human albumin migrates towards the anode there is an electro-osmotic flow of buffer solutions towards the cathode. It has been found that Whatman 3MM. paper is satisfactory in reducing this flow to the desired minimum. The physician's diagnosis is confirmed by an increase of gamma globulin and some decrease in albumin, both of which are revealed by simple inspection. The paper strip method brings electrophoretic analysis well within the scope of normal clinical laboratory routine, and compares very favourably with previous techniques on cost, time and accuracy.

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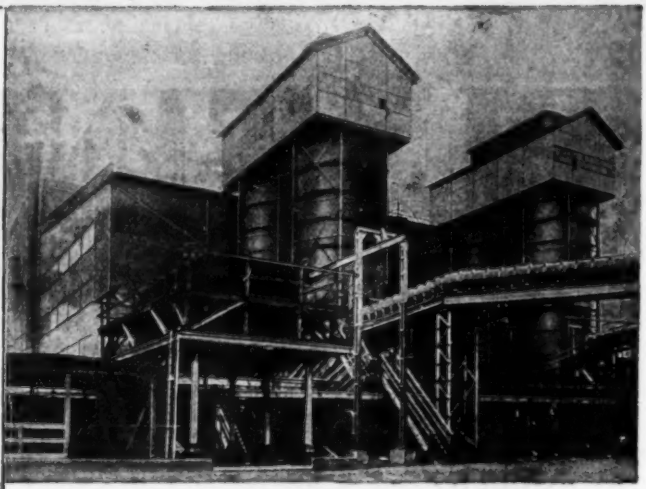

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ON THE STUDY OF INDIRECT APPLICATION OF RADIOACTIVE NUCLEI IN ANALYTICAL CHEMISTRY

By B. C. Purkayastha and V. R. Pai Verneker

It has been shown that through indirect method of analysis by radioactive nuclei, elements of γ order of magnitude can be estimated with a fair degree of accuracy. In the present investigation the estimation of Ag and I_2 has been undertaken using I^{131} as a measuring indicator. The principle involved in such estimations is as follows: Excess of iodine (double or triple the theoretical equivalent amount of Ag) as KI containing I^{131} is added to unknown Ag in acid solution; the trace of AgI is completely precipitated and is carried along with zirconium phosphate. From the loss in activity of I^{131} in the filtrate, the amount of Ag present can be calculated. With a known amount of Ag, unknown iodide can also be estimated under the same condition It has been found that even one microgram (10^{-6} g.) of Ag can be estimated with statistical accuracy ($\pm$ 2 %) within half an hour. Zirconium phosphate has been found a faithful carrier of AgI. It carries AgI even beyond the solubility limit. It appears that by the use of a suitable carrier a much lower limit than that reached by radiometric titration is always achieved.

As an extension to our study on indirect radiochemical estimation, the determination of weakly basic elements by allowing hydrolysis to completion with IO_3^---I^- mixture, was taken up. Aluminium up to the limit of 40γ (40×10^{-6} g.) has thus been estimated with a fair degree of accuracy within 2 hours Possible application of this principle to routine chemical analysis has also been discussed.

Most of the radiochemical estimations can be classified under two main heads, namely, either by process of activation in accelerators or reactors or by indirect applications of radioactive indicators. Though the first procedure is very sensitive in most of the cases, and in favourable circumstances even up to 10^{-12} g. of elements can be estimated, it is not always possible to have a reactor beside and conduct day to day analysis; so the second procedure of indirect radiochemical analysis also plays an important role in our every day laboratory work. Specially during the last few years, chemical analysis by radiometric titrations (Alimarin, "International Conference on Peaceful Uses of Atomic Energy", 1955, **15**, p. 60) has become popular and is finding extensive applications. It is going to replace the earlier method of indirect estimation by precipitating a fraction of the element with its radioactive isotope under investigation and measuring the loss in activity. In spite of various advantages, sensitivity and limit of analysis by radiometric titration are conditioned by the solubility of the compound precipitated. It was Sue (*Bull. soc. chim.*, 1946, *v*, **15**, 103) who first attempted to overcome the solubility factor by carrying the invisible precipitate formed by a scavenger.

In his attempt to estimate silver, he took some known amount of KI and impregnated it with I^{131}; he then added the micro amount of the silver salt to be estimated and carried this small amount of AgI precipitate by addition of $Fe(OH)_3$, prepared by addition of NaOH to $FeCl_3$ solution. He found that carrying was in most of the cases 98% up to the extent of 10^{-5} g. of silver, and beyond it there was incomplete carrying of AgI. (Even with 10 μg. he got a negative error of about 10% in some cases). From

such considerations it seems that use of any scavenger may not lead us to counterbalance the solubility and other sources of errors associated with the estimation of micro amounts.

The main object of the present investigation is to find out a reagent that can coprecipitate AgI whereby a better degree of accuracy in much lower concentration in case of Ag and I can be achieved. Of the common substances, insoluble in acids with tolerable surface adsorption, zirconium phosphate, barium sulphate etc. come to mind. In the present investigation, zirconium phosphate has been used as a carrier of ultramicro quantities of AgI. It has been found to behave as a faithful carrier of AgI and high precision in the estimation of Ag and I in ultramicro quantities can be arrived at. The principle involved in such estimations is as follows: Excess of iodine (double or triple the theoretical equivalent amount of Ag) as KI containing I^{131} is added to unknown Ag in acid solution; the trace of AgI is completely precipitated and carried along with zirconium phosphate. From the loss in activityof I^{131} in the filtrate, the amount of Ag present can be calculated. In case we take a known amount of Ag, an unknown iodide can also be estimated under the same conditions.

The second objective of our study is to extend and apply I^{131} in the determination of weakly basic elements by allowing hydrolysis to completion with KIO_3-KI mixture.

It is well known that the salt of a weakly basic element undergoes hydrolysis. If the hydrogen ion formed is progressively removed by some mechanism then in favourable circumstances hydrolysis becomes perfectly complete. Removal of the hydrogen ion in the present investigation has been carried out by the well-known iodate-iodide reaction.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$$

The iodine liberated can be distilled and collected in alkaline sodium sulphite (or better in $N/10$-NaOH) and estimated in case of large quantities by isotopic dilution and in case of small quantities, by adding a known amount of Ag and carrying it along with zirconium phosphate. Aluminium in potash alum has been taken as a representative of weakly basic elements.

EXPERIMENTAL

The reagents $AgNO_3$, KI, potash alum, KIO_3, Na_2SO_3, Na_2CO_3 and NaH_2PO_4 were all of G. R. E. Merck quality. The carrier-free I^{131} as supplied by Messers Philips Roxane was used. Zirconium nitrate of BDH (L.R.) was treated several times with perchloric acid and it was finally tested and found free from chloride and nitrate. It was kept in acid solution. Description of a typical experiment as given below will clarify the procedure adopted.

Estimation of Ag *and* I.—Ag as $AgNO_3$ of the order of a few micrograms was taken in a beaker. To the solution about three times the amount of iodine required by the equation

$$AgNO_3 + KI \rightarrow AgI + KNO_3$$

was added. Previous to this addition carrier-free I^{131} and I^{127} were thoroughly mixed; zirconium (~ 1 mg.) perchlorate was added; the solution as a whole was about $0.1N$ in

acidity. To this solution sodium dihydrogen phosphate solution was added in slight excess and the mixture was warmed for a few minutes till coagulation was complete. Zirconium phosphate together with coprecipitated AgI was then filtered through a naphthalene bed, and from the activity remaining in the filtrate, the amount of I_2 or Ag, as the case may be, was estimated. In most of the cases the measurements were done with a liquid counter under standard conditions. The volume in case of γ order of magnitude was not allowed to exceed 20 c.c. during the time of precipitation, and it was found that washing with 15 c.c. of water was sufficient to remove the excess iodide. In half an hour the whole operation including the activity measurements can be completed. Previous to the actual estimation, a study was made on the adsorption of I^{131} on zirconium phosphate (vide Table I). In case of estimation of Ag (vide Table II), a known amount of KI was added as mentioned above, and in case of unknown I_2 (vide Table III), a known quantity of Ag was added. The data are recorded in a tabular form.

Estimation of Aluminium.—Potash alum was dissolved in H_2SO_4 (dil.) in such volume that the concentration of the latter did not go below 0.2*N*. Aluminium in solution was analysed by oxine method according to Knowles (*J. Res., NBS*, 1935, **15**, 87). The concentration of free acid was known from the known amount of acid added ; this was also confirmed by determining free acid in presence of aluminium by the known method by titrating free acid with alkali in presence of excess $Na_2C_2O_4$. Purity of the alum was further tested by determining aluminium sulphate ratio. This was taken for a stock solution.

TABLE I

Adsorption of varying quantities of iodide on different amounts of zirconium phosphate.

No.	Zr taken.	Vol. of precipitating medium.	I_2 taken in μg. (10^{-6} g)	% I adsorbed.
1.	2.5 mg.	30 c.c.	0.00 (without carrier)	87
2.	2.5	30	7.78	12
3.	2.5	30	23.34	0
4.	2.5	30	389.00	0
5.	1.0	30	7.78	8
6.	1.0	30	11.67	0
7.	1.0	30	15.50	0
8.	1.0	30	23.34	0
9.	0.5	15	3.89	20
10.	0.5	15	7.78	0
11.	0.5	15	7.78	0

TABLE II

Estimation of Ag.

No.	Experimental condition.	Silver in μg (10^{-6} g.). Taken.	Found.	Standard deviation in activity measurement.
1.	6 mg. of Zr in 200 c.c.	187.6	189.0	±2%
2.	,,	3.53	3.50	±1 8
3.	,,	3.53	3.63	±3.4
4.	1 mg of Zr in 40 c.c.	172	170	±2.0
5.	,,	22 75	22.95	±2.0
6.	,,	32.78	32.18	±2.2
7.	,,	11.38	11.30	±2.0
8.	,,	9.00	9.08	±1.8
9.	,,	3.682	3.555	±3.4
10.	0.5 mg Zr in 15 c.c.	1.67	1.658	±1.5
11.	,,	1.67	1.658	±1.5
12.	,,	1.67	1.660	±1.5
13.	,,	1.67	1.680	±1.5
14.	,,	1.67	1.650	±1.5
15.	,,	0.835	0.844	±1.5
16.	,,	0.835	0.826	±1.5

The error is always within statistical fluctuation as shown above.

TABLE III

Estimation of iodine.

No.	Experimental condition	Iodine in (mμg × 10^{-6} g.). Taken.	Found.	Standard deviation in activity measurement.
1.	1 mg of Zr in 30 c.c.	389.0	401 0	±2.2%
2.	,,	389.0	395.0	±2.2
3.	,,	77.8	77.03	±2.0
4.	,,	38.9	38.10	±2.0
5.	,,	38.9	38.73	±2.0
6.	,,	15.56	15.58	±1.8
7.	,,	15.56	16.11	±2.0
8.	6 mg. of Zr in 200 c.c.			
	,,	778	794	±2.5
9.	,,	778	777	±1.5
10.	,,	23.34	23.48	±2.0
11.	,,	15.56	15.15	±2.5
12.	0.5 mg. of Zr in 15 c.c.			
	,,	7.78	7.90	±2.0
13.	,,	7.78	7.839	±2.0
14.	,,	7.78	7.839	±2.0
15.	,,	7.78	7.88	±2.0
16.	,,	7.78	7.80	±2.0

Error as shown above is always within statistical fluctuation.

An aliquot portion of the stock solution containing about 23 mg. of aluminium was taken in an one-litre round bottomed flask fitted with a standard glass joint. Volume was made about 300 c.c. KI (~ 5 g.) and KIO_3 (~ 5 g.) were added and the flask was fitted to a delivery system including a condensing arrangement. On boiling, iodine was liberated with progressive hydrolysis and collected in a conical flask containing a solution of sodium sulphite or caustic soda, and cooled by ice to avoid escape of any iodine. In the case of estimating iodine by titrating against hypo, iodine was collected in a concentrated solution of potassium iodide, free from iodine. In case of micro-estimations, iodate-iodide was first added to water and two thirds volume distilled to drive out any free iodine which might be present in iodate or iodide. Double distilled water was all along used. The precision of the arrangement was tested by adding a known amount of sulphuric acid and estimating the iodine distilled. Aluminium was estimated by titrating iodine against hypo and also as AgI gravimetrically. To simplify the procedure of gravimetric estimation, iodine collected was labelled with I^{131} and estimation was done by isotopic dilution. In case of trace of aluminium, indirect procedure, as described above, was adopted.

TABLE IV

Estimation of aluminium by classical chemical methods.

No.	Aluminium (in mg.) Taken.	Found.	Amount of IO_3^- and I^- used in 300 c.c.	No.	Aluminium (in mg.) Taken.	Found.	Amount of IO_3^- and I^- used in 300 c.c.	No.	Aluminium (in mg.) Taken.	Found.	Amount of IO_3^- and I^- used in 300 c.c.
1.	0.4674	0.4680(v)*	1g. KI 1g. KIO_3	7.	23.37	23.71(v)*	5g. KI 10g. KIO_3	12.	116.8	117.0(v)*	5g. KI 10g. KIO_3
2.	0.4674	0.4723(v)*	Do	8.	23.37	23.57(v)*	Do	13.	116.8	116.95(v)*	Do
3.	2.337	2.344(v)*	1g. KI 2g. KIO_3	9.	70.11	69.10(v)*	,,	14.	4.674	4.657(G)*	1g. KI 2g. KIO_3
4.	2.337	2.344(v)*	1g. KI 1g. KIO_3	10.	116.80	115.2(v)*	,,	15.	4.674	4.614(G)*	Do
5.	4.674	4.647(v)*	1g. KI 2g. KIO_3	11.	116.80	116.1 v)*	,,	16.	23.370	23.420(G)*	5g. KI 10g. KIO_3
6.	4.674	4.672(v)*	Do					17.	23.370	23.145*(G)	Do

v*—Iodine was collected in a solution of iodine-free iodide (10 g.) in a conical flask cooled in ice. Glass wool on the mouth of the flask was used as a preventive measure. Two thirds of the volume was distilled and titrated against hypo.

G*—Iodine was absorbed in 0.4 g. of sodium sulphite and 0.1 g. of sodium carbonate and estimated gravimetrically as AgI.

TABLE V

Estimation of aluminium by the use of I^{131}.

No.	Aluminium (mg.) Taken.	Found.	Amount of IO_3^- and I^- used in 300 c.c.	No.	Aluminium (mg.) Taken.	Found.	Amount of IO_3^- and I^- used in 300 c.c.
1.	3.2116	3.136(D)* ±2.5%	0.5 g. KI 0.5 g. KIO_3	6.	0.13764	0.1400(R)* ±2.3%	0.5 g. KI 0.5 g. KIO_3
2.	4.588	4.506(D)* ±2.3%	Do	7.	0.18352	0.1870(R)* ±2.2%	Do
3.	0.04588	0.04543(R)* ±2.2%	,, ,,	8.	0.22440	0.2290(R)* ±2.3%	,, ,,
4.	0.04588	0.4544(R)* ±2.2%	,,	9.	0.4588	0.4685(R)* ±2.3%	,,
5.	0.09176	0.09045(R)* ±2.0%	,,	10.	1.3764	1.3730 R)* ±2.2%	,,

D*—Iodine was absorbed in 0.4 g. of sodium sulphite and 0.1 g. of sodium carb nate; I^{131} was added, thoroughly mixed and precipitated as CuI after neutralisation and mounted on a counting tray and estimaied by isotopic dilution.

R*—Iodine was collected in sodium sulphite and sodium carbonate and slowly neutralised. Nearly one third equivalent of known silver was added and silver iodide was carried by zirconium phosphate following the same procedure as described in our experiment (by radiometric estimation).

DISCUSSION

The data on the estimation of Ag (Table II) show that very small quantities of Ag, even 10^{-6} g., can be estimated with a fair degree of accuracy within a very short time. The limit can be further extended beyond even a microgram if we can either make correction for surface adsorption of iodide ion at such low concentrations on Zr phosphate or overcome the adsorption factor by adding still lower quantities of Zr. But in such cases conditions, volume, etc. should also be changed.

One of the interesting aspects of the use of zirconium phosphate is that AgI is coprecipitated even beyond its solubility limit. Zirconium phosphate should not therefore be treated as a simple collector of invisible precipitate, but it is actually a coprecipitating agent; whereas $Fe(OH)_3$, as used by Sue, seems to be a collector; we have also found that it has got its limitations depending upon the iodine ion concentration in the solution. We are not yet certain why zirconium phosphate is such a faithful carrier of AgI, but we are hopeful that use of a carrier, which does not interfere with the excess of the consitituents, will always lead us to a lower limit of estimation. The principle promises a better degree of accuracy than that can be achieved by estimating an element by radiometric titration and other indirect procedures. I^{131} was chosen as a preliminary start because of its popular use everywhere and its applications in the field of studies other than the insoluble iodides. Tables IV and V show that iodometric estimation of aluminium is a very convenient method. From general volumetric point of view, we are to take recourse to the

most popular hypo titration which is very accurate and very rapid. In case of gravimetric estimation, silver iodide is about twenty-six times the weight of aluminium taken ; so the factor is very favourable for micro-determination of aluminium in the gravimetric way. In case of beryllium, equivalent amount of silver iodide will be forty-seven times the weight of beryllium. It is therefore very tempting for micro-chemists to run after this procedure. Question naturally arises whether we can apply this method to our day to day routine chemical analysis. The answer depends on the question of estimation of free acid by depressing the hydrolysis of weak bases in question or by some other means as has been done in the case of aluminium. It will form a subject matter of a separate study, specially in case of micro-determination.

It should be further noted that in case of high activity handling this method of determining weak bases will be very useful in a general chemical laboratory. It is of general interest whether this type of estimation will be of use to industry where the cost of reagents is also taken into account. We are quite confident that iodide and iodate can be used once and once again. Even the small quantity of zirconium, which has been used as carrier of AgI in estimating trace quantities of aluminium, can also be recovered and used again ; the method is very simple and does not take more than two hours. Table IV describing the results of indirect radiochemical analysis will show that we did not go beyond 4×10^{-5} g. aluminium (40μ g.). It has been found by us that iodine liberated below this concentration of aluminium is rather high ; many causes may be attributed to this high result. Our study in this aspect is still incomplete.

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THE BEHAVIOUR OF ELECTROLYTES IN MIXED SOLVENTS. PART II. VISCOSITY OF POTASSIUM CHLORIDE IN METHYL ALCOHOL — WATER MIXTURERS AT 35°

By K. Singh, P. K. Das and D. Patnaik

The present investigation comprises the study of viscosity of KCl solutions in 10, 20, 30, 40 and 50% by weight of MeOH-H_2O mixtures. The experimental data fit in well with the Jones-Dole equation:

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC.$$

While up to 30% composition B does not show any significant change with the composition of the solvent, its dependence on the composition of the solvent has been observed in the case of 40% and 50% mixtures. The nature and the composition of the sphere of solvation are suggested to be responsible for the magnitude of B.

In extension of our previous investigation (this *Journal*, 1957, **34**, 56) we have examined the viscosity behaviour of potassium chloride in methyl alcohol-water mixtures.

Experimental

Potassium chloride and methyl alcohol used were of E. Merck 'extra pure' quality. KCl was purified as described previously (*loc. cit.*). Traces of water from methyl alcohol were removed by putting it in contact with freshly fired CaO for 4 days. It was distilled and was immediately put to use: the first and the last fractions were always rejected. The other experimental details have been described before (*loc. cit.*).

Table I

Temp. = 35°.

Conc. (g. mol./litre).	η/η_0.	$1+A\sqrt{C}$.	BC.	B.	η/η_0.	$1+A\sqrt{C}$.	BC.	B.
	MeOH : H_2O = 50 : 50.		A = 0.0071.		MeOH : H_2O = 40 : 60.		A = 0.0065.	
0.010	1.0014	1.0007	0.0007 g.	0.070	1.0006	1.0007	...	...
0.025	1.0025	1.0011	0.0014	0.056	1.0013	1.0010	0.0003	0.012
0.050	1.0045	1.0016	0.0029	0.058	1.0022	1.0014	0.0008	0.016
0.075	1.0064	1.0020	0.0044	0.059	1.0031	1.0018	0.0013	0.017
0.100	1.0083	1.0023	0.0050	0.060	1.0040	1.0020	0.0020	0.020
0.125	1.0101	1.0025	0.0076	0.061	1.0048	1.0023	0.0025	0.020
0.150	1.0119	1.0028	0.0091	0.061	1.0056	1.0025	0.0031	0.021
0.175	1.0137	1.0030	0.0107	0.061	1.0065	1.0027	0.0038	0.022
0.200	1.0155	1.0032	0.0123	0.061	1.0073	1.0029	0.0044	0.022
			Mean	0.061			Mean	0.020

TABLE I (contd.)

[M and H refer respectively to MeOH and H_2O]

*Conc. (g. mol./litre).	η/η_0.	$1+A\sqrt{C}$.	BC.	η/η_0.	$1+A\sqrt{C}$.	BC.	η/η_0.	$1+A\sqrt{C}$.	BC.
	M:H = 30:70.		$A=0.058$.	M:H = 20:80.		$A=0.0054$.	M:H = 10:90.		$A=0.0051$.
0.010	1.0001	1.0006	−0.0005	1.0001	1.0005	−0.0004	1.0005	1.0005	...
0.025	1.0005	1.0009	−0.0004	1.0005	1.0009	−0.0004	1.0008	1.0008	...
0.050	1.0011	1.0013	−0.0002	1.0004	1.0012	−0.0008	1.0011	1.0011	...
0.075	1.0016	1.0016	±0.000	1.0007	1.0015	−0.0008	1.0015	1.0014	0.0001
0.100	1.0022	1.0018	0.0004	1.0008	1.0017	−0.0009	1.0016	1.0016	0.0003
0.125	1.0022	1.0021	0.0001	1.0013	1.0019	−0.0006	1.0018	1.0018	...
0.150	1.0028	1.0023	0.0005	1.0016	1.0021	−0.0005	1.0022	1.0020	0.0002
0.175	1.0030	1.0024	0.0006	1.0019	1.0025	−0.0006	1.0022	1.0021	0.0001
0.200	1.0033	1.0026	0.0007	1.0019	1.0024	−0.0005	1.0022	1.0023	−0.0001

TABLE II

Temp. = 35°.

Conc. (g. mol./litre).	Λ ohms^{-1}.	Λ_0 ohm^{-1}.	Λ ohms^{-1}.	Λ_0 ohm^{-1}.	Λ ohms^{-1}.	Λ_0 ohm^{-1}.	Λ ohms^{-1}.	Λ_0 ohm^{-1}.	Λ ohms^{-1}.	Λ_0 ohm^{-1}.
	M:H = 50.50.		M:H = 40.60		M:H = 30.70.		M:H = 20.80.		M:H = 10:50.	
0.0100	90.80	—	91.90		103.70		116.8		139.2	
0.0075	91.35		93.40		104.30		117.7		139.5	
0.0050	91.90	94.6	93.90	97.5	105.05	108.7	118.6	124.2	139.7	141.3
0.0025	92.55		94.85		106.10		120.1		139.95	
0.0010	94.30		95.80		106.90		121.3		140.5	
										180.42 *

* The figure refers to the zero composition of the mixture *i.e.*, containing only water (Benson and Gordon, *J. Chem. Phys.*, 1945, **13**, 473).

DISCUSSION

The relative viscosity η/η_0 for each of the concentrations of KCl in different mixtures was directly determined. For the evaluation of the constant A of the Jones-Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

the dielectric constant data given by Åkerlöf (*J. Amer. Chem. Soc.*, 1932, **54**, 4125) and the conductance data shown in Table II have been used. The value of B was estimated for each concentration of the electrolyte on substitution of the calculated value of A and the measured value of η/η_0 in equation (1). The results are represented in Table I. From these data it can be seen that there is no regular change in the product BC with the change of concentration of KCl in solvents containing methyl alcohol up to 30% ; but the product BC shows a regular change with the concentration in cases of solvents containing 40% and 50% of methyl alcohol. This behaviour can be satisfactorily explained by assuming that B has no significant contribution up to 30% composition of methyl alcohol. For such compositions, the equation (1) reduces to $\eta/\eta_0 = 1 + A\sqrt{C}$.

It has been reported by Chakravarti (this *Journal*, 1943, **20**, 41) that the constant B is almost zero for aqueous solutions of KCl at 35°. Therefore it can safely be stated that the behaviour of KCl solution in these mixed solvents up to 30% of methyl alcohol is similar to that of water. A positive value of B for 40% and 50% composition of methyl alcohol indicates that the Jones-Dole equation containing the term BC is applicable for higher composition mixtures.

From our study of viscosity of KCl solutions in dioxane-water mixtures (*loc. cit.*), we are of opinion that the magnitude of B is related to the nature of the sphere of solvation. The inadmissibility of the term involving B for 10, 20 and 30% composition mixtures indicates that the nature of the sphere of solvation is not materially altered by the presence of methyl alcohol molecules. The same conclusion has been arrived at by Amis (*J. Phys. Chem.*, 1956, **60**, 428) from his study of the conductance of KCl in MeOH-H_2O mixtures. At higher compositions of the solvent the MeOH molecules play a significant part in determining the nature and composition of the sphere of solvation. This expectation is justified by the fact that there is a regular increase in the value of B with the increase in the composition of the non-aqueous solvent, as has been observed in 40% and 50% mixtures.

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ESTIMATION OF FORMALDEHYDE BY ROMIJN'S METHOD IN PRESENCE OF AMMONIUM SALTS

By S. Bose

In the hypoiodite oxidation method of estimating formaldehyde, ammonium salts interfere. A mixture of 3% mercuric chloride and about 40% potassium iodide has been found to prevent completely this interference. The usual black precipitate, produced by the action of hypoiodite on ammonium salts, does not appear; the solution remains clear and excellent results are obtained for formaldehyde.

Romijn's method (*Z. anal. Chem.*, 1897, **36**, 19) of estimating formaldehyde consists in treating formaldehyde solution with a definite volume of standard iodine solution and an excess of sodium hydroxide solution. The excess of iodine is estimated by acidifying the reaction mixture with hydrochloric acid and titrating the liberated iodine with hypo, using starch as indicator. Although the method is good, it is not applicable to dilute solutions containing formaldehyde and ammonium salts. When the reaction mixture is made alkaline, ammonia reacts with hypoiodite, affording a black precipitate of indefinite composition consisting of a mixture of NI_3 and $NI_3.NH_3$ (Ephraim, "Inorganic Chemistry", 1939, p. 738). Even a trace of ammonium salt takes up a large amount of iodine and the interference is profound.

Dilute solutions of formaldehyde and ammonium salts react very slowly at room temperature to form hexamethylenetetramine and the reaction soon attains an equilibrium because of the reverse reaction becoming more prominent with the increase in acidity. The acid is produced by the complete hydrolysis of the tetramine salt on account of its very weak basicity.

$$4\ NH_4Cl + 6HCHO \rightleftharpoons (CH_2)_6N_4 + 4\ HCl + 6\ H_2O$$

If the solution is made alkaline, the rate of formation of tetramine increases; the maximum rate has been observed at p_H 8 by Polley, Winkler and Nicholls (*Canadian J. Res.*, 1947, **25B**, 525). In Romijn's method excess of sodium hydroxide is used. In presence of ammonium salts the formaldehyde not only undergoes oxidation but also reacts with the ammonia produced by the excess of alkali. This constitutes the second interference produced by ammonium salts

It has been found that on addition of a solution of mercuric chloride, containing a large excess of potassium iodide, to the formaldehyde solution, the interferences produced by ammonium salts are completely prevented.

Ammonia probably forms a complex with $K_2(HgI_4)$. Nicholls and Willits (*J. Amer. Chem. Soc.*, 1934, **56**, 769) consider that the composition of the Nessler's precipitate is $NH_2Hg_2I_3$ which is, however soluble in excess of KI. In the present procedure of estimation due to the addition of a large excess of potassium iodide, no precipitate appears, and the complex formed with ammonia remains in solution. Thus, ammonia is prevented from reacting with either hypoiodite or formaldehyde.

Bougault and Gros (*J. pharm. chim.*, 1922, **26**, 5) have described a method of estimating formaldehyde by oxidation with alkaline Nessler's solution. After keeping

for 15 minutes or more, a greyish yellow precipitate appears consisting of mercury and mercurous salts, which are quantitatively reoxidised by acidified iodine solution, the excess of iodine being titrated back with hypo. In the present method, where alkaline Nessler's solution containing excess of potassium iodide has been used, the reaction mixture remains clear throughout and no precipitate appears. Hence, the oxidant here is the sodium hypoidite and not the Nessler's solution. Moreover, it has been found that alkaline Nessler's solution, containing excess of potassium iodide, oxidises formaldehyde very slowly, producing a pure grey precipitate of mercury, and in 20 minutes only 25% of the aldehyde is oxidised. In presence of hypoiodite the oxidation is complete in 20 minutes. Sodium hypoiodite appears to be a more powerful oxidising agent, and hence, acts as the oxidant in the method described.

EXPERIMENTAL

Procedure.—The solution of a mixture of mercuric chloride and potassium iodide was prepared freshly by dissolving 3 g. of mercuric chloride in 100 c.c. of water and adding to it 50 g. of potassium iodide. The solution had a slight yellowish tinge and was used on the same day. Both the chemicals used were pure. The formaldehyde solution (5 c.c.) to be estimated was taken by a pipette in a pyrex conical flask of 100 c.c. capacity. The concentration of formaldehyde was 0.1 *M* and that of ammonium chloride, 0.05*M* or less. About 8 c.c. of $HgCl_2$-KI solution was added to the conical flask along with 12.5 c.c. of standard 0.1*N* iodine solution from a burette. The reaction mixture was made alkaline by adding 2 c.c. of 1*N*-NaOH from a graduated pipette. The conical flask was corked and kept for at least 20 minutes at about 20°. It was shaken several times during this period. Finally its contents were acidified with 4 c.c. of 1*N*-HCl and the iodine liberated was titrated with 0.05*N*-hypo solution. A blank was run simultaneously, similar in all respects except for the addition of formaldehyde solution. The difference in the hypo readings gave the formaldehyde present in the mixture (1 c.c. of 0.05*N*-hypo solution = 0.75 mg. of HCHO).

Table I records the results of analysis of mixtures of 0.2*M* formaldehyde and 0.1*M* ammonium chloride in various proportions. In all the mixtures the final concentration of formaldehyde was 0.1 *M*. The actual value for formaldehyde was determined by double diluting the 0.2 *M* solution with water and estimating by Romijn's method. All mixtures were prepared fresh and immediately estimated.

TABLE I

H.CHO actually present = 20 c.c.

Conc. of NH_4Cl present.	$HgCl_2$-KI soln. added to 5 c.c. of mixture.	H.CHO found.	Error.
(1) Nil	Nil	...	...
(2) *M*/40	5 c.c.	19.95 c.c.	−0.25%
(3) *M*/30	5	19.95	−0.25
(4) *M*/20	8	20.0	±0.0
(5) *M*/15	10	20.05	+0.25
(6) *M*/10	10	20.05	+0.25

(From 2 to 6 the I_2 added is 30% to 35% in excess of what is required).

Interference due to Large Excess of I_2.—Romijn's method as modified by Singer (*Helv. Chim. Acta*, 1930, **13**, 43) lays down that I_2 added should be at least double the amount actually required. Experiments were carried out with pure solutions of formaldehyde to assess the minimum amount of excess of I_2 required for complete oxidation of formaldehyde in presence of $HgCl_2$-KI solution. The results as presented in Table II show that about 33% in excess is enough to afford constant and correct values for the aldehyde.

TABLE II

In each experiment 5 c.c. of 0.075 *M*-HCHO was estimated and the amount of NaOH added was 2 c.c. of 1*N* solution. H.CHO actually present = 15.0 c.c.

$HgCl_2$-KI solution added.	*N*/20-I_2 added.	I_2 added in excess.	H.CHO found.	%Error.
Nil	30 c.c.	15 c.c. (100%)	15.00 c.c.	±0.0
,,	25	10 (66%)	14.95	−0.35
,,	20	5 (33%)	14.40	−4.0
,,	18	3 (20%)	14.00	−6.5
8 c.c.	18	3 (20%)	14.50	−3.5
8	20	5 (33%)	14.95	−0.35

When a large excess of I_2 was used for estimating mixtures of ammonium chloride and formaldehyde, higher values for the aldehyde were obtained. It was found that 33% − 50% I_2 in excess furnished good results.

TABLE III

[5 c.c. of a mixture of 0.075*M*.HCHO and 0.05 *M*-NH_4Cl estimated with 0.1 *N* iodine solution using 1*N* NaOH (2 − 3 c.c.) and 0.05 *N*-hypo.]

Conc. of NH_4Cl = 0.05*M*. H.CHO actually present = 15.0 c.c. $HgCl_2$ − KI soln. added = 8 c.c.

0.1-*N*-I_2 added.	I_2 in excess.	H.CHO found.	%Error.
10 c.c.	2.5 c.c. (33%)	15.05 c.c.	+0.33
12	5.5 (73%)	15.10	+0.66
15	7.5 (100%)	15.40	+2.6
20	12.5 (166%)	16.00	+6.6

Mixtures of HCHO, NH_4Cl *and* $(CH_2)_6N_4$ *Analysed*.—Dorer and Ozimic (*Farm. Glasnik*, 1949, **5**, No. 9/10,174) state that Romijn's hypoiodite method of estimating formaldehyde is applicable in presence of hexamethylenetetramine. The present method using $HgCl_2$ − KI solution was also found to be successful in presence of tetramine as elucidated in Table IV. The concentration of formaldehyde in the mixture was 0.075 *M*.

TABLE IV

Conc. of NH_4Cl soln. = 0.05*M*.

Conc. of hexamethylene-tetramine.	$HgCl_2$-KI soln. added to 5 c.c. of the mixture.	HCHO present.	HCHO found.
0.1 *M*	8 c.c.	15.0 c.c.	14.95 c.c.
0.2	8	15.0	14.95
0.4	8	15.0	14.95

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COLORIMETRIC ESTIMATION OF CHLORAL (HYDRATE)

By O. P. Malhotra and V. D. Anand

The Fujiwara colour reaction has been extended to the estimation of chloral (hydrate). Different factors influencing the intensity and stability of colour have been studied. The intensity of colour exhibits a linear relationship with the amount of chloral (hydrate). The method is free from interference by common impurities in chloral hydrate.

The Fujiwara colour reaction between chloroform, pyridine and strong alkalies at 100° (*Sitzungsber. Abhandl. naturforsch. Ges. Rostock*, 1914, **6**, 1) was found by Ross to be a general test for compounds with -C (halogen)$_3$ moiety (*J. Biol. Chem.*, 1923, **58**, 641). Various workers applied this reaction for the colorimetric estimation of chloroform and carbon tetrachloride in blood and tissues of animals, air and soil (Cole, *ibid.*, 1926, **71**, 173 ; Gettler and Blume, *Arch. Path.*, 1931, **11**, 554 ; Daroga and Pollard, *J. Soc. Chem. Ind.*, 1941, **60**, 218 ; Adams, *J. Pharmacol.*, 1942, **74**, 11 ; Kulkarni, *Curr. Sci.*, 1943, **12**, 324 ; *Indian J. Med. Res.*, 1944, **32**, 189 ; Ussing, *Acta Physiol. Scand.*, 1945, **9**, 214 ; Habgood and Powell, *Brit. J. Ind. Med.*, 1945, **2**, 39 ; Webb, Kay and Nichol, *J. Ind. Hyg. Toxicol.*, 1945, **27**, 249). As chloral contains the -C (halogen)$_3$ group and is known to be readily and quantitatively hydrolysed to chloroform, it has been thought of interest to extend this method to the estimation of chloral (cf. Friedman and Calderone, *J. Lab. Clin. Med.*, 1934, **19**, 1332).

Previous workers showed that with chloroform or carbon tetrachloride, best results were obtained with 20% NaOH and that a brighter colour was produced in the presence of acetone (Daroga and Pollard, *loc.cit.*). These conditions have been found satisfactory and therefore maintained in the following experiments. The colour was ordinarily unstable, but could be stabilised for a longer period by cooling and separating the coloured pyridine layer, although different orders of stability have been reported by different workers. Similarly, several different periods of heating have been recommended in the literature. The present studies were therefore carried out with reference to the following variants :

(*i*) The influence of heating time on colour intensity.
(*ii*) The stability of red colour after separating the coloured pyridine layer.
(*iii*) The variation of colour intensity with the amount of chloral hydrate using technical and pure pyridine.
(*iv*) The influence of impurities in chloral on colour intensity.

A heating time of 5 minutes was found to be optimum and the colour was stable for over one hour. There was straight line relationship between the quantity of chloral and the colour intensity with technical as well as pure pyridine ; the latter, however, exhibited a more intense colour and was therefore more suited when very small quantities of chloral were to be estimated. Such common impurities as hydrochloric acid, ethanol and dichloracetaldehyde did not interfere with the reaction.

EXPERIMENTAL

Influence of Heating Time on Colour Intensity.—A mixture of 5 c.c. of 40% NaOH* solution, 10 c.c. of colorless technical pyridine bases (b.p. 115°-40°), 2 c.c. of acetone and 5 c.c. of aqueous test solution (2.42 mg. of $CCl_3.CHO$, H_2O) was heated with shaking in a 50 c.c. r.b. flask, plugged with cotton wool on a boiling water-bath for varying intervals of time (2-6 mins.). After cooling under tap water (about 20°) for 1-2 minutes, the coloured pyridine layer was separated and diluted with acetone to 20 c.c. in a measuring flask. A 10 mm layer of this solution was matched against glass standards in a Lovibond tintometer. The results are recorded in Table I.

TABLE I

Time of heating (mins.)		2	3	4	5	6
Reading	Red	4.5	4.6	4.9	4.9	4.9
	Brightness	0.2	0.2	0.2	0.2	0.2

The colour intensity being maximum at 4-6 minutes, an optimum heating time of 5 minutes was therefore adopted for the subsequent experiments.

Stability of Red Colour.—The above experiment was repeated with a heating time of 5 minutes and the final diluted coloured solution matched as before in the tintometer at different intervals of time (Table II).

TABLE II

Time after separation (mins.)		5	15	30	60	120	180
Reading	Red	4.9	4.9	4.9	4.9	4.6	4.3
	Brightness	0.2	0.2	0.2	0.2	0.2	0.2

Thus, the colour was stable for more than one hour. A more thorough separation by settling the pyridine layer for a longer period did not improve the stability. It only exhibited a brighter colour (brightness 0.4), probably due to a more complete removal of suspended globules of alkali solution from the pyridine layer.

Variation of Colour Intensity with the amount of Chloral Hydrate.—To 40% NaOH (5 c.c.), colorless technical pyridine bases (b.p. 115-40° ; 10 c.c.) and acetone (2 c.c.) in a 50 c.c. r.b. flask were added varying amounts (*i*) (0.5-5.0 c.c.) of chloral hydrate solution (0.9680 mg./c.c.) and (*ii*) water (4.5-0.0 c.c.) so that the total volume of (*i*) and (*ii*) added was always 5 c.c. The reaction mixture was treated as before and a 10 mm depth of the final diluted coloured solution matched in the tintometer. The results have been summarised in Table III and represented in Fig. 1.

* The total volume of aqueous layer (5 c.c. NaOH + 5 c.c. test solution) came to 10 c.c. so that the final solution was 20% NaOH.

TABLE III

With tech. pyridine bases (b.p. 115–40°).
Tot l vol. added = 5.0 c.c.

S. No.	Chloral hydrate added.		Water added.	Tintometer reading.	
	Soln.	Amount.		Red.	Brightness.
1	0.5 c.c.	0.484 mg.	4.5 c.c.	0.9	0.2
2	1.0	0.968	4.0	1.9	0.2
3	1.5	1.452	3.5	2.7	0.2
4	2.0	1.936	3.0	3.8	0.2
5	2.5	2.420	2.5	4.8	0.2
6	3.0	2.904	2.0	5.8	0.2
7	3.5	3.388	1.5	6.7	0.2
8	4.0	3.872	1.0	7.6	0.2
9	4.5	4.356	0.5	8.6	0.2
10	5.0	4.840	0.0	9.5	0.2

A similar set of experiments was carried out with chemically pure pyridine (b.p. 112-14°) taking 1-5 c.c. of a weaker solution of chloral hydrate (0.1936 mg./c.c.) because the above stronger solution gave large values of intensities (more than 20 Lovibond units) with pure pyridine (Table IV, Fig. 1).

TABLE IV

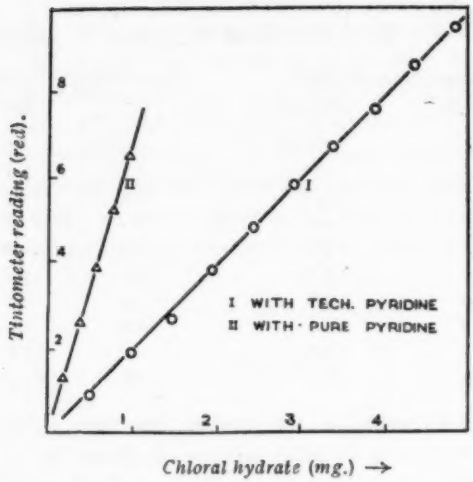
With chemically pure pyridine.
Total vol. added = 5.0 c.c.

S. No.	Chloral hydrate added.		Water added.	Tintometer reading	
	Soln.	Amount.		Red.	Brightness.
1	1.0 c.c.	0.1936 mg.	4.0 c.c.	1.3	0.1
2	2.0	0.3872	3.0	2.6	0.1
3	3.0	0.5808	2.0	3.9	0.1
4	4.0	0.7744	1.0	5.2	0.1
5	5.0	0.9680	0.0	6.5	0.1

The Influence of Impurities on Colour Intensity.—Several experiments were performed with 2-3 mg. of chloral hydrate when present alone and also in mixtures with 1-4 mg. of dichloroacetaldehyde, 10-20 mg. of HCl and 20-40 mg. of ethanol. The colour intensity was not affected by any one or all of these impurities.

The colour produced by heating chloral hydrate with NaOH and pyridine has maximum intensity for a heating time of 4-6 minutes and can be stabilised for more than one hour by cooling and separating the coloured pyridine layer ; it is quantitatively reproducible. On plotting the intensity of red colour against the amount of chloral hydrate, a straight line is obtained with technical as well as pure pyridine, indicating the applicability of Beer's law to the system (Fig. 1). The common impurities such as dichloroacetaldehyde, hydrochloric acid and ethanol do not interfere.

FIG. 1



For equal quantities of chloral hydrate, however, a more intense colour is developed with pure pyridine than with the technical variety (e.g. 6.5 and 1.9 Lovibond red units respectively for 0.9680 mg. of $CCl_3.CHO.H_2O$, cf. Fig. 1). This is in conformity with an earlier observation of Daroga and Pollard (*loc.cit.*) that with $CHCl_3$ or CCl_4 the colour developed is a function of the amount of pyridine added. Thus, whereas both technical and pure pyridine can be used for this estimation, the latter is preferable when very small amounts of chloral are to be estimated.

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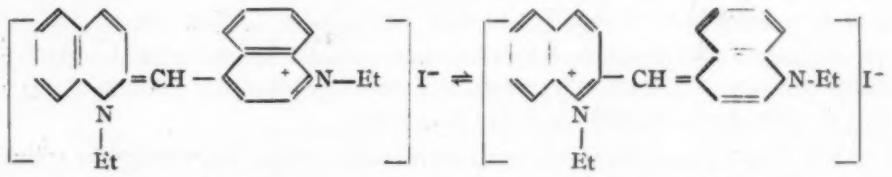
CYANINE DYES. PART I

By Bhaskar Das and M. K. Rout

Six thiazolo-carbocyanine dyes derived from 4-phenyl-, 4-*p*-methoxyphenyl-, 4-*p*-ethoxyphenyl-, 4-*p*-bromophenyl-, 4-*p*-nitrophenyl-2-methylthiazole and 2-methylbenzothiazole have been prepared in two ways, viz., (*i*) by reaction with ethyl orthoformate and (*ii*) with the help of acetanilidovinyl intermediates.

The majority of the sensitising dyes are drawn from the group, known collectively as polymethines, of which cyanines constitute a very important group and are characterised by the presence of two basic nuclei linked together through a conjugated chain of carbon atoms, as shown in the structure (I) of a typical example.

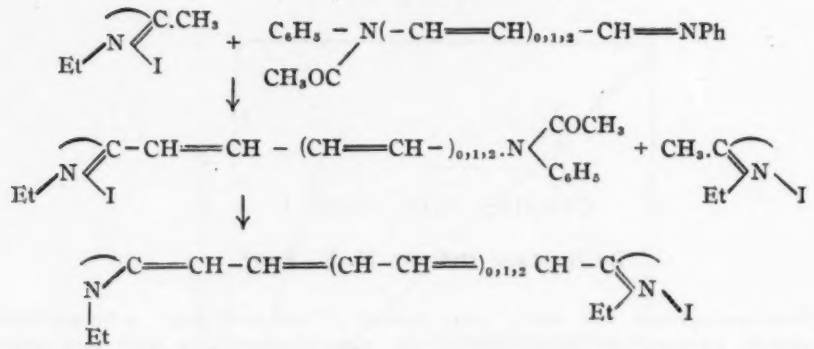


(I) (II)

The cationic charge can, however, be associated with either of the two heterocyclic nitrogens, thus giving rise to a second structure (II).

Since both the structures are identical and equally probable, the positive charge must be shared equally between the two nitrogens. It necessariiy implies that the nitrogen atoms must be joined by an even number of linkages, half of them single bonds and half of them double bonds, and in passing from one 'extreme' (as it is called) structure to the other, the arrangement of linkages in the chain is reversed, as shown above.

The nuclei which have been widely used in the preparation of cyanine dyes are quinoline, pyridine, benzothiazole, benzoxazole and benzselenazole. Thiazoles have not, however, received considerable attention. The present investigation deals with a few cyanines derived from substituted thiazoles. These have been prepared in two ways: (*i*) by reaction of two proportions of methyl quaternary salt with one proportion of ethyl orthoformate; ethyl alcohol and hydrogen iodide are eliminated in the process; and (*ii*) by reaction of a molecule of the quaternary salt with an intermediate of the dianilide type and subsequent condensation of the resulting product with another molecule of the quaternary salt.



The sensitisation spectra and the absorption maxima of these dyes have been measured and will be reported elsewhere.

EXPERIMENTAL

4-Phenyl-2-methylthiazole was prepared according to the method of Hantsch (*Ber.*, 1888, **21**, 943) and obtained in 78% yield (Hantsch did not record the yield of his compound). Doja and Banerjee (this *Journal*, 1946, **23**, 222) record the yield as 80%, m.p. 68°. (Found : C, 68.40 ; H, 4.39. Calc. for $C_{10}H_9NS$: C, 68.57 ; H, 4.11%).

4-Phenyl-2-methylthiazole methiodide was prepared by the method of Mills and Smith (*J. Chem. Soc.*, 1922, **121**, 2735), m.p. 202°, yield 65%. (Found : C, 41.48 ; H, 3.60. Calc. for $C_{11}H_{12}NIS$: C, 41.64 ; H, 3.78%).

3 : 3'-Dimethyl-4 : 4'-diphenylthiazolo-carbocyanine iodide was prepared by refluxing the preceding methiodide (3.17 g.) and ethyl orthoformate (0.74 g.) in pyridine (10 c.c.) for 2 hours. Excess of pyridine was removed by distillation under reduced pressure. The dark residue on being treated with ether was kept in contact with methyl alcohol. Crystallisation from hot methyl alcohol furnished dark needles with greenish violet reflex, m.p 187° (decomp.), yield 50%. (Found : C, 53.27 ; H, 3.89. $C_{23}H_{21}N_2IS_2$ requires C, 53.48 ; H, 4.06%).

4-p-Nitrophenyl-2-methylthiazole was prepared by the condensation of ω-bromo-*p*-nitroacetophenone with thioacetamide in benzene medium, m.p. 118°, yield 75%. (Found : C, 54.37 ; H, 3.51. $C_{10}H_8O_2N_2S$ requires C, 54.55 ; H, 3.63%).

4-p-Nitrophenyl-2 methylthiazole Methiodide.—The above 2-methylthiazole (2.20 g.) and methyl iodide (1.42 g.) were heated in a sealed tube for 30 hours. The product was washed with cold water repeatedly, treated with ether and finally recrystallised from hot methanol in light yellow needles, m.p. 186° (decomp.), yield 63%. (Found : C, 36.25 ; H, 2.89. $C_{11}H_{11}O_2N_2IS$ requires C, 36.46 ; H, 3.03%).

3 : 3'-Dimethyl-4 : 4'-di-(p-nitrophenyl)-thiazolo-carbocyanine Iodide.—The preceding methiodide (3.62 g.) and ethyl orthoformate (0.74 g.) were refluxed in pyridine (15 c.c.) for 3 hours. Excess of pyridine was removed by distillation under reduced pressure and the dark product was treated with ether. When crystallised twice from hot methanol, the product separated as shining blue prisms, m.p. 191° (decomp.), yield 45%. (Found : C, 45.32 ; H, 3.03. $C_{23}H_{19}O_4N_4IS_2$ requires C, 45.54 ; H, 3.13%).

4-p-*Methoxyphenyl-2-methylthiazole* was obtained by the condensation of *p*-methoxyphenacyl bromide with thioacetamide, m.p. 63°, yield 65%. (Found: C, 64.24 ; H, 5.21. $C_{11}H_{11}ONS$ requires C, 64.39 ; H, 5.36%).

4-p-*Methoxyphenyl-2-methylthiazole methiodide* was prepared by the same method as described in case of other methiodides, m.p. 198°, yield 50%. (Found : C, 41.33 ; H, 3.87. $C_{12}H_{14}ONIS$ requires C, 41.51 ; H, 4.03%).

3 : 3′-*Dimethyl*-4 : 4′-*di*-(p-*methoxyphenyl*)-*thiazolo-carbocyanine Iodide*.—The above methiodide (3.47 g.) and ethyl orthoformate (0.74 g.) were refluxed in pyridine (10 c.c.) for nearly two hours and following the same method as described before, a slight gummy product was obtained. It was treated with ether, followed by acetone, to remove tarry products and was then recrystallised from hot methanol, m.p. 183° (decomp.), yield 50%. (Found : C, 51.82 ; H, 4.18. $C_{25}H_{25}O_2N_2IS_2$ requires C, 52.08 ; H, 4.34%).

4-*p*-Ethoxyphenyl-2-methylthiazole and its methiodide, 4-*p*-bromophenyl-2-methylthiazole and its methiodide and 2-methylbenzothiazole methiodide were prepared and their m.p., yield and analytical data have been reported elsewhere.

3 : 3′-*Dimethyl*-4 : 4′-*di*-(p-*ethoxyphenyl*)-*thiazolo-carbocyanine iodide* was prepared in the usual way (*vide supra*) from a mixture of the preceding methiodide (3.61 g.) and ethyl orthoformate (0.74 g.) in pyridine (15 c.c.) for 2 hours. It crystallised from hot methanol in deep reddish violet needles, m.p. 172° (decomp.), yield 48%. (Found : C, 53.52 ; H, 4.97. $C_{27}H_{29}O_2N_2IS_2$ requires C, 53.64 ; H, 4.80%).

3 : 3′-*Dimethyl*-4 : 4′-*di*-(p-*bromophenyl*)-*thiazolo-carbocyanine iodide* was prepared as above from 4-*p*-bromophenyl-2-methylthiazole methiodide (3.96 g.) and ethyl orthoformate (0.74 g.) in pyridine (15 c. c.). The pure material was obtained by two recrystallisations from hot methanol in dark red crystals, m.p. 240° (decomp.), yield 48%. (Found : C, 40.78; H, 2.65. $C_{23}H_{19}N_2Br_2IS_2$ requires C, 40.94 ; H, 2.81%).

3 : 3′-*Dimethyl*-4 : 4′-*dibenzothiazolo-carbocyanine Iodide*.—A mixture of 2-methylbenzothiazole methiodide (2.91 g.) and ethyl orthoformate (0.74 g.) in pyridine (10 c.c.) was refluxed for 90 minutes. After removing excess of the solvent by distillation under reduced pressure, the product was treated with ether. The pure material was obtained by two recrystallisations from hot methanol in deep red-violet crystals with blue reflex, m.p. 265° (decomp.), yield 50%. (Found : C, 49.02 ; H, 3.51. $C_{19}H_{17}N_2IS_2$ requires C, 49.13 ; H, 3.66%).

2-(2-*Acetanilidovinyl*)-4-*phenylthiazole methiodide* was prepared by refluxing 4-phenyl-2-methylthiazole methiodide (3.17 g., 1 *M*) and diphenyl formamidine (1.96 g., 1 *M*) in acetic anhydride (15 c.c.) for 60 minutes. Excess of acetic anhydride was removed by distillation under reduced pressure and the product was treated with ether. The product after being washed with water was treated with acetone to remove tarry products. The acetone-washed product was sufficiently pure for further reactions. The pure material was obtained by recrystallising the substance from hot methanol, m. p. 162-63° (decomp.), yield 52%. (Found : C, 51.78 ; H, 4.02 $C_{20}H_{19}ON_2IS$ requires C, 51.95 ; H, 4.10%).

3 : 3'-Dimethyl-4 : 4'-diphenylthiazolo-carbocyanine iodide was prepared from the above methiodide (4.62 g., 1 *M*) and 4-phenyl-2-methylthiazole methiodide (3.17 g. 1*M*) by refluxing in ethanol (15 c.c.) with triethylamine (1.01 g., 1 *M*) in a steam-bath for an hour. On cooling, the product separated as dark crystals. On crystallisation from methyl alcohol the product separated in dark needles with greenish violet reflex, m.p. 187° (decomp.), yield 48%. (Found : C, 53.50 ; H, 4.29. $C_{23}H_{21}N_2IS_2$ requires C, 53.48 ; H, 4.06 %).

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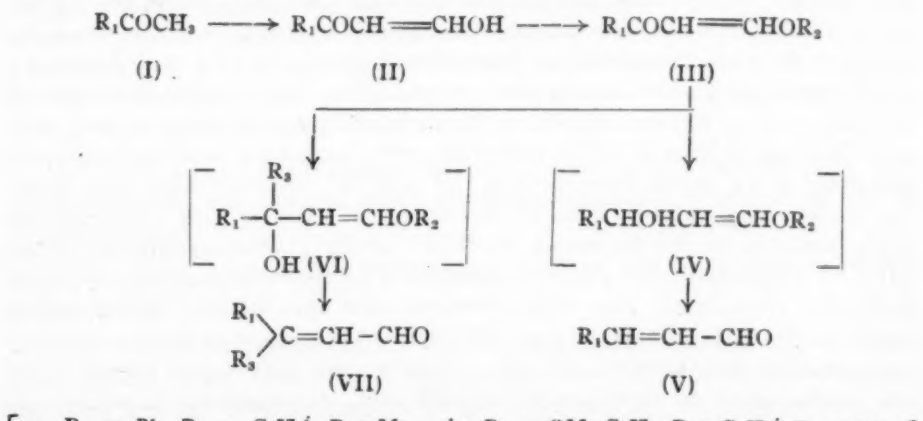
A CONVENIENT ROUTE TO αβ-UNSATURATED ALDEHYDES

By R. P. Gandhi, J. S. Walia and S. M. Mukherji

The Seifert and Schinz method for *cyclo*alkenyl aldehydes has been extended to the synthesis of αβ-unsaturated aldehydes of aralkyl as well as aliphatic series. Convenient preparations of cinnamaldehyde, β-methyl-, *p*-methoxy- and β-methyl-*p*-methoxy-cinnamaldehydes, β-methylcrotonaldehyde and β-(6-methoxy-2-naphthyl)-acraldehyde are described.

Our interest in the study of the Michael reaction of αβ-unsaturated aldehydes with ethyl acetoacetate (Mukherji and Bhattacharyya, this *Journal*, 1946, **23**, 451) as a promising route to steroidal hormone derivatives led us to search for a convenient general method for the preparation of αβ-unsaturated aldehydes in the arylalkyl and aliphatic series. Literature records a number of methods for the purpose (Groschientz and Fisher, *J. Amer. Chem. Soc.*, 1941, **63**, 2021; Von Braun and Rudolph, *Ber.*, 1934, **67**, 269, 1735; Wittig and Kethur, *Ber.*, 1936, **69**, 2078; Kröhnke and Börner, *Ber.*, 1936, **69**, 2006; Kröhnke, *Ber.*, 1938, **71**, 2583; Young and Linden, *J. Chem. Soc.*, 1947, 2913; Arens and Van Drop, *Nature*, 1947, **160**, 189; Heilbron *et al.*, *J. Chem. Soc.*, 1949, 737, 291; Seifert and Schinz, *Helv. Chim. Acta*, 1951, **34**, 728). However, the procedure recently elaborated by Seifert and Schinz (*loc. cit.*) appears, because of its simplicity and adaptability, to be eminently suited for the synthesis of a wide variety of αβ-unsaturated aldehydes. The present communication reports the preliminary experiments conducted with a view to seeking a logical extension of Seifert and Schinz's original method (*loc. cit.*). By making use of the modified procedure, a practicable preparative route to a number of αβ-unsaturated aldehydes such, as cinnamaldehyde, β-methyl-, *p*-methoxy-β-methyl- and *p*-methoxy-cinnamaldehydes, β-methylcrotonaldehyde and β-(6-methoxy-2-naphthyl)-acraldehyde has been developed. The reaction sequence employed is schematically represented below.



[a: R_1 = Ph, R_2 = $C_4H_9^i$, R_3 = Me. b: R_1 = OMe.C_6H_4, R_2 = $C_4H_9^i$, R_3 = Me.
c: R_1 = R_3 = Me, R_2 = $C_4H_9^i$. d: R_1 = OMe.$C_{10}H_6$, R_2 = Me]

Acetophenone and *p*-methoxyacetophenone were converted into the corresponding ω-hydroxymethylene derivatives (IIa and IIb) under Birch's conditions (*J. Chem. Soc.*, 1944, 501) in 60% and 35% yield respectively. Claisen and Stylos (*Ber.*, 1889, **21**, 1144) reported acid-catalysed self-condensation of hydroxymethylene-acetophenone, but in our hands it was considerably obviated by avoiding distillation and using the crude hydroxymethylene derivative for the next operation. In the case of other formyl derivatives, excepting formylacetone, no such difficulty was encountered. The formyl compounds, (IIa and IIb), on subsequent treatment with *iso*butanol in the presence of *p*-toluenesulphonic acid in refluxing benzene (Salmi, *Ber.*, 1938, **71**, 1803; cf. Surber and Schinz, *Helv. Chim. Acta*, 1954, **37**, 1239), produced ω-*iso*butoxymethylene-acetophenone (IIIa) and ω-*iso*butoxymethylene-*p*-methoxy-acetophenone (IIIb) in 73% and 74% yield respectively. These underwent smooth reduction with lithium aluminium hydride to the corresponding carbinols, (IVa and IVb) (not isolated) which, on acid hydrolysis under Seifert and Schinz's conditions (*loc. cit.*), furnished cinnamaldehyde (Va) and *p*-methoxycinnamaldehyde (Vb) in 76% and 77% yield respectively.

A variant of the reduction step was sought in the Grignard reaction on the alkoxymethylene ketone, the intermediary carbinol (VI) being capable of undergoing anionotropic rearrangement (cf. Seifert and Schinz, *loc. cit.*). This constitutes another simple approach to ββ-disubstituted-αβ-unsaturated aldehydes. Accordingly, (IIIa) and (IIIb) were allowed to react with methylmagnesium iodide and the Grignard compounds hydrolysed directly, as above, to β-methylcinnamaldehyde (VIIa) and β-methyl-*p* methoxycinnamaldehyde (VIIb) in 55% and 88% yield respectively. The two-stage process *via* the intermediate carbinols (VIa) and (VIb) resulted in diminished yields.

The method was then adapted to the preparation of β-methylcrotonaldehyde. Literature records a few recent syntheses of this important *iso*prenoid aldehyde (Mukherji, this *Journal*, 1948, **25**, 163; Wendler and Slates, *J. Amer. Chem. Soc.*, 1950, **72**, 5341; Heilbron and Weedon, *J. Chem. Soc.*, 1949, 1823; Young and Linden, *loc. cit.*) which, however, are seriously handicapped from the preparative standpoint because of the relative complexity of experimental operations. The present method is only a two-stage process starting from acetone. The dimethylacetal from hydroxymethylene-acetone, prepared according to Royals and Brannock (*J. Amer. Chem. Soc.*, 1953, **75**, 2050), on being allowed to react with methylmagnesium iodide and subsequent hydrolysis of the intermediate carbinol (not distilled) under Wendler and Slates' (*loc. cit.*) conditions, afforded β-methylcrotonaldehyde (VIIc) in 41% yield. Another similar procedure for the preparation of (VIIc) employed *iso*butoxymethylene-acetone (IIIc). Formylacetone was prepared according to the conditions prescribed by Boileau (*Bull. Soc. chim.*, 1954, 761) using chloroacetic acid, thus avoiding self-condensation reported by Claisen (*Annalen*, 1894, **278**, 274). The preparation of *iso*butoxymethylene-acetone by Salmi's method (*loc. cit.*) resulted in a low yield (25%) because of the low boiling point of formylacetone coupled with its insolubility in benzene and possibility of self-condensation. However, *iso*butoxymethylene-acetone (IIIc) could be transformed smoothly in good yield (59%) to β-methylcrotonaldehyde through

similar reactions. Again, 6-methoxy-2-acetylnaphthalene (Id) was converted into its methoxymethylene derivative (IIId) by a procedure similar to that of Royals and Brannock (*loc. cit.*) in 41% yield. This was then reduced in dioxane with lithium aluminium hydride and subsequently hydrolysed under Seifert and Schinz's (*loc. cit.*) conditions to β-(6-methoxy-2-naphthyl)-acraldehyde (Vd) in 56% yield. The orange-red colour of the 2 : 4-dinitrophenylhydrazone derivative is indicative of the αβ-nature of unsaturation in (Vd).

EXPERIMENTAL

ω-Hydroxymethylene-acetophenone (IIa).—To molecularised sodium (23 g., 1*M*) under anhydrous ether was introduced dropwise a mixture of acetophenone (120 g., 1 *M*) and ethyl formate (84 g., 1.2 *M*), in cold. After the addition was complete, the contents were left standing overnight and then worked up in the usual manner, when a mobile oil was obtained which resisted distillation. The crude material weighed 100 g. (60%). It developed an intense violet coloration with alcoholic ferric chloride.

ω-iso*Butoxymethylene-acetophenone* (IIIa).—A mixture of the above crude formyl compound (56 g.), *iso*butanol (84 g.), and a little *p*-toluenesulphonic acid in anhydrous benzene (200 c.c.) was refluxed using a Dean and Stark water separator till no more water collected. To the contents was then added a little sodium ethoxide to neutralise the excess acid, followed by a sufficient quantity of water. On working up in the customary way, a colorless mobile oil was collected at 150°/6 mm, yield 52 g. (73%). (Found : C, 76.11 ; H, 7.56. $C_{13}H_{16}O_2$ requires C, 76.44 ; H, 7.90%). It gradually developed a violet coloration with alcoholic ferric chloride.

Cinnamaldehyde (V).—To a well-stirred, fine suspension of lithium aluminium hydride (2.44 g.) in anhydrous ether (200 c.c.) was added dropwise ω-*iso*butoxy-methylene-acetophenone (IIIa : 20 g.) at a rate such as to maintain ether at gentle reflux. After the addition was complete, the contents were refluxed for another 15 minutes. Excess hydride was decomposed with 10 c.c. of water. The contents were then treated at 0°-5° with a mixture of sulphuric acid (39.5 c.c.) and ice (30 g.) for one hour. The hydrolysate on working up in the customary manner yielded 10 g. (75.7%) of cinnamaldehyde, b.p. 130°/20 mm.

The 2 : 4-*dinitrophenylhydrazone* derivative, after repeated crystallisations from glacial acetic acid, melted at 251° which remained undepressed on admixture with an authentic sample.

The melting point of the semicarbazone alone as well as when mixed with an authentic sample was 207°.

β-Methylcinnamaldehyde (VIIa).—The Grignard reagent was prepared from magnesium (2.48 g.), methyl iodide (14.5 g.) and dry ether (120 c.c.) and to this was introduced, under ice cooling, ω-*iso*butoxymethylene-acetophenone (IIIa : 20.4 g.) over a period of 20 minutes and the mixture left standing overnight. The contents were decomposed with H_2SO_4 (40 c.c.) and ice (30 g.) at 0°-5°, and the hydrolysate was extracted with

ether. After removal of the solvent the residue was distilled at 130°/12 mm as a colorless oil, yield 8 g. (55%). (Found: C, 82.10; H, 7.09. Calc. for $C_{10}H_{10}O$: C, 82.16; H, 7.09%).

The 2:4-*dinitrophenylhydrazone* derivative was obtained as orange-red needles, which, after crystallisation from glacial acetic acid, melted at 231°. (Found: N, 17.50. $C_{16}H_{14}O_4N_4$ requires N, 17.17%).

The *semicarbazone* was crystallised from ethanol as greyish white needles, m.p. 198; lit. m.p. 201° (Heilbron, "Dictionary of Organic Compounds", 1946, p. 647). (Found: N, 21.2. Calc. for $C_{11}H_{13}ON_3$: N, 20.7%).

ω-Hydroxymethylene-p-methoxyacetophenone (IIb).—A mixture of *p*-methoxyacetophenone (0.5 *M*. 75 g.), and ethyl formate (0.6 *M*, 42 g.) was dropped with good shaking to powdered sodium (0.5 *M*, 11.5 g.) under anhydrous ether (400 c.c.), in the cold. The contents after being allowed to stand overnight were treated in the manner of (IIa) when 30 g. (34%) of ω-hydroxymethylene-*p*-methoxyacetophenone (IIb) was obtained as a light oil, distilling at 135°/10 mm. It developed a deep violet coloration with alcoholic ferric chloride.

ω-iso*Butoxymethylene*-p-*methoxyacetophenone* (IIIb).—A mixture of the above formyl compound (IIb: 28 g.), *iso*butanol (25 g.) and little *p*-toluenesulphonic acid in benzene (250 c.c.) was treated in the same manner as in the case of (IIIa). The *iso*butoxymethylene derivative (IIIb) distilled at 155°/10 mm as a colorless oil, yield 25 g. (74%). It showed a violet coloration with alcoholic ferric chloride on keeping or warming. (Found: C, 71.60; H, 7.70. Calc. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69%).

p-*Methoxycinnamaldehyde* (Vb).—*ω-iso*Butoxymethylene-*p*-methoxyacetophenone (IIIb: 10 g.) was reduced with lithium aluminium hydride (1.47 g.) in anhydrous ether (150 c.c.) in the manner analogous to that in the case of (Va), when 5 g. (77%) of *p*-methoxycinnamaldehyde (Vb) was obtained, distilling at 145°/7 mm. (Found: C, 74.51; H, 6.66. Calc. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22%).

The 2:4-*dinitrophenylhydrazone* was crystallised from ethyl acetate as orange-red needles, m.p. 210°. (Found: N, 16.60. $C_{16}H_{14}O_5N_4$ requires N, 16.37%).

The *semicarbazone* was crystallised from ethanol as colorless needles, m.p. at 196°. Lit. m.p. 199° (Beilstein, "Organische Chemie", 1925, Vol. VIII, p. 130). (Found: N, 19.30. Calc. for $C_{11}H_{13}O_2N_3$: N, 19.15%).

β-Methyl-p-*methoxycinnamaldehyde* (VIIb).—To the Grignard reagent, prepared from magnesium (1.2 g.), methyl iodide (7.1 g.) and anhydrous ether (100 c.c.), was introduced, in cold, *ω-iso*butoxymethylene-*p*-methoxyacetophenone (11.7 g.) in dry ether (25 c.c.). The Grignard complex was worked up in the manner of (VIIa) to obtain *β*-methyl-*p*-methoxycinnamaldehyde (VIIb) as a colorless mobile oil, b.p. 150-52°/10 mm, yield 7.8 g. (8%). (Found: C, 74.22; H, 6.85. $C_{11}H_{12}O_2$ requires C, 74.97; H, 6.86%).

The 2:4-*dinitrophenylhydrazone* derivative was deposited as red needles which, after crystallisation from acetic acid melted at 224°. (Found: N, 15.70. $C_{17}H_{16}O_5N_4$ requires N, 15.72%).

The *semicarbazone* crystallised from ethanol as colorless needles, m.p, 194°. (Found: N, 18.20. $C_{12}H_{15}O_2N_3$ requires N, 18.02%).

β-Methylcrotonaldehyde (VIIc).—The dimethylacetal of formylacetone was obtained from acetone exactly according to the method prescribed by Royals and Brannock (*loc. cit.*).

The Grignard reagent was prepared from magnesium (1.67 g.), methyl iodide (9.8 g.) and anhydrous ether (100 c.c.) and to this was introduced, dropwise and under ice-cooling, the above acetal (9.2 g.) in dry ether (25 c.c.). The contents after being allowed to stand overnight were decomposed with saturated ammonium chloride solution and the organic material was taken up in ether. After removal of solvent the residual oil was treated with 5% H_2SO_4 (120 c.c.) and alcohol (10 c.c.), warmed for 5 minutes and then allowed to stand at room temperature for 10 hours. The usual working up of the hydrolysate furnished 2.4 g. (41%) of a colorless oil, b.p. 130-35°. (Found: C, 71.50; H, 9.66. Calc. for C_5H_8O: C, 71.39; H, 9.59%).

The 2:4-*dinitrophenylhydrazone* derivative, after crystallisation from ethyl acetate, melted at 180°. Lit. m.p. 183° (Wendler, *loc. cit.*). (Found: N, 21.40. Calc. for $C_{11}H_{12}O_4N_4$: N, 21.20%).

iso*Butoxymethylene-acetone* (IIIc).—A mixture of formylacetone (35 g.) (Boileau, *loc. cit.*), *iso*butanol (30 g.), a little *p*-toluenesulphonic acid in anhydrous benzene (100 c.c.) was heated to gentle reflux for 2 hours and then refluxed vigorously till there was no more separation of the lower layer in the separator (which consisted of unchanged formylacetone and water). The contents were treated in the manner analogous to that in the case of (IIIa) to obtain 13.3 g. (25%) of (IIIc) as colorless mobile oil, b.p. 102-105°/7 mm. It gradually developed a violet colour with alcoholic ferric chloride. (Found: C, 67.75; H, 9.9. $C_8H_{14}O_2$ requires C, 67.60; H, 9.85%). In certain runs, however, no *iso*butoxymethylene-acetone could be collected.

β-Methylcrotonaldehyde (VIIc).—The above *iso*butoxy compound (6.9 g.) in dry ether (25 c.c.) was treated with the Grignard reagent, prepared from magnesium (1.17 g.), methyl iodide (7 g.) and anhydrous ether (75 c.c.), in cold. On working up in the manner similar to that in the case of dimethylacetal of hydroxymethylene-acetone, 2.4 g. (59%) of β-methylcrotonaldehyde was obtained, b.p. 130-35°.

The 2:4-*dinitrophenylhydrazone* derivative melted at 180° and remained undepressed on admixture with the sample from the above experiment.

ω-*Methoxymethyl-6-methoxy-2-acetylnaphthalene* (IIId).—6-Methoxy-2-acetylnaphthalene (Id) was prepared according to the procedure of Robinson and Rydon (*J. Chem. Soc.*, 1939, 1399).

A mixture of (Id: 40 g.) and ethyl formate (18 g.) in dry benzene (200 c.c.) was added gradually, under ice-cooling, to powdered sodium (4.6 g.) covered with anhydrous benzene (200 c.c.). After 24 hours' standing, the thick brown mass was filtered and the residue washed repeatedly with anhydrous ether. The dried sodium salt weighed 45 g. (90%). To the cooled suspension of the dry salt (40 g.) in absolute methanol (36 g.) was introduced, with vigorous stirring, a cold solution of dry hydrogen chloride (15 g.) in anhydrous methanol (28 g.). After one hour's additional stirring, the contents were left standing for 4 hours at 20°. Methyl alcoholic potassium

hydroxide was added to make the mass just alkaline whereafter it was filtered and the residue washed with methanol. The filtrate yielded 15 g. (41%) of (IIId), as a highly viscous oil, b.p. 198-200°/7 mm. (Found: C, 74.70; H, 5.93. $C_{13}H_{14}O_2$ requires C, 74.4; H, 5.78%).

β-(6-Methoxy-2-naphthyl)-acraldehyde (Vd).—To a well-stirred suspension of lithium aluminium hydride (1.425 g.) in dry dioxane (150 c.c.) was introduced gradually a solution of (IIId: 10 g.) in dioxane (50 c.c.). After 20 hours' refluxing, the contents were worked up as in (Va) to obtain 5.5 g. (56%) of a colorless immobile oil, b.p. 215-20°/5 mm. (Found: C, 79.10; H, 6.0. $C_{14}H_{12}O_2$ requires C, 79.22; H, 5.70%).

The 2:4-*dinitrophenylhydrazone* derivative was prepared in the customary way and crystallised from ethyl acetate as orange-red needles, m.p. 228°. (Found: N, 14.00. $C_{20}H_{16}O_5N_4$ requires N, 14.28%).

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A NEW SYNTHESIS OF *cis*-8-METHYLHYDRINDANONE-1

By Ramesh Chandra Chatterjee and Bidyut Kamal Bhattacharyya

A new synthesis of *cis*-8-methylhydrindanone-1 has been described.

In the classical synthesis of equilenin, Johnson and his co-workers (*J. Amer. Chem. Soc.*, 1947, **69**, 2942) built up the *cyclo*pentane ring from 1-keto-2-methyl-2-cyano-7-methoxy-1:2:3:4-tetrahydrophenanthrene by the Stobbe condensation with dimethyl succinate. Attempts to apply this reaction with other similar systems resulted either in cleavage of the ring containing the nitrile or the elimination of carbomethoxy group (*ibid.*, 1950, **72**, 1426; 1952, **74**, 2832; "Organic Reactions", Vol. VI, p. 13).

In order to circumvent the above difficulties in the Stobbe-Johnson reaction, an attempt in the following line was made to obtain the desired propionic acid chain, keeping the carbomethoxy group at 2-position intact (cf. *Science & Culture*, 1956, **21**, 543).

Ethyl 2-methyl*cyclo*hexanone-2-carboxylate (I: R = Me; $R_1 = CO_2Et$) underwent the Knoevenagel condensation with ethyl cyanoacetate by the procedure of Cope *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 3452) as modified by Ciagoe *et al.* (*J. Org. Chem.*, 1950, **15**, 381) to furnish ethyl 2-methyl-2-carbethoxy*cyclo*hexylidene-1-cyanoacetate (II: R = Me; $R_1 = CO_2Et$) in 60-66% yield. This compound was previously prepared by Linstead and Millidge (*J. Chem. Soc.*, 1936, 478) in poor yield.

During the afore-mentioned condensation, a solid byproduct has been obtained which is resistant to acid hydrolysis but can be hydrolysed with 20% aqueous sodium hydroxide solution (Kon and Thorpe, *ibid.*, 1919, **115**, 686; Paul, this *Journal*, 1931, **8**, 717) to furnish the unsaturated dicarboxylic acid (XVI: m.p. 169°) which is the β-acid of Bachmann and Kushner (*J. Amer. Chem. Soc.*, 1943, **65**, 1963). The authentic sample of the dicarboxylic acid (XVI) has been prepared from the unsaturated cyano-ester (II: R = Me; $R_1 = CO_2Et$) by hydrolysis with hydrochloric acid. The structure (III) has been assigned to the byproduct on the basis of the above evidence and its ultraviolet data (*Ann. Rep. Chem. Soc.*, 1945, **42**, 105; Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76; cf. Banerjee *et al.*, *J. Org. Chem.*, 1954, **19**, 1516; Sukh Dev, this *Journal*, 1953, **30**, 443; Chaudhuri and Mukharji, *ibid.*, 1956, **33**, 155).

The unsaturated cyano-ester (II: R=Me; $R_1 = CO_2Et$) was then condensed with ethyl bromoacetate in presence of sodium ethoxide according to the procedure of Cope *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 3458) to yield diethyl α-cyano-α-(2-methyl-2-carbethoxy*cyclo*hex-Δ^{6}-enyl)-succinate (IV: R=Me; $R_1 = R_4 = CO_2Et$; $R_2 = Et$; $R_3 = CN$). The latter compound on hydrolysis with concentrated hydrochloric acid yielded either a mixture of acids (A: m.p. 152-53°) and (B: m.p. 184-85°) or an oily mixture of acids (A) and (B) containing a solid acid (C: m.p. 200°) depending upon the period of heating. The gummy acidic residue left after fractional crystallisation was esterified to furnish a mixture of the neutral tri-ester (IV: $R=R_2=Me$; $R_1=R_4=CO_2Me$; $R_3=H$) and the lactonic di-ester (V: $R=Me$; $R_1=R_2=CO_2Me$).

The acid (A) could be converted by treatment with diazomethane into the above neutral ester and the latter could be saponified back to the acid (A), which from its analytical and neutral equivalent data should have the structure (IV: R=Me; $R_1=R_4=CO_2H$; $R_2=R_3=H$). Further, the acid (A) could be converted, in poor yield, either into the acid (B) or the acid (C), depending on the period of heating with concentrated hydrochloric acid.

The above-mentioned lactonic di-ester was saponified to the acid (B) which could again be esterified with diazomethane to the same ester. The latter on treatment with sodium methoxide in methanol and methyl iodide, followed by treatment with dilute hydrochloric acid, yielded the tri-ester (IV: $R=R_2=Me$; $R_1=R_4=CO_2Me$; $R_3=H$). Hence, the probable structure (V: R=Me; $R_1=R_2=CO_2H$) may be assigned to the acid (B).

The acid (C) from its neutral equivalent and conversion to the methyl ester with diazomethane has been found to be a lactonic monocarboxylic acid and may have any one of the structures (V: R=Me; $R_1=CO_2H$; $R_2=H$ and R=Me; $R_1=H$; $R_2=CO_2H$); (X: R=Me; $R_1=CO_2H$; $R_2=H$ and R=Me; $R_1=H$; $R_2=CO_2H$); (XII) and (XIII). It was treated with phosphorus pentachloride followed by alcohol and the crude chloro compound, thus formed, was then heated with zinc and acetic acid (Mukherji, this *Journal*, 1947, **25**, 449), but the result was unpromising. The chloro-ester was next refluxed with alcoholic potassium hydroxide solution (10, 25 and 40%) to get the unsaturated dicarboxylic acid, but unfortunately a resinous material was obtained in each case. Finally, a methanolic solution of the acid (C) on treatment with sodium methoxide and methyl iodide yielded a hydroxy-ester which on dehydration with fused potassium hydrogen sulphate, followed by hydrogenation, furnished a saturated di-ester. The latter on hydrolysis furnished a dicarboxylic acid, m.p. 156° which may have either the structure (XVII: R=Me; $R_1=CO_2H$; $R_2=R_3=H$) or (XIV: $R=R_1=H$). Both the *cis*- and *trans*-forms of the acid (XVII: R=Me; $R_1=CO_2H$; $R_2=R_3=H$) have been prepared by Johnson (*J. Amer. Chem. Soc.*, 1944, **66**, 215); the *cis*-acid, m.p. 108-109°, and the *trans*-acid, m.p. 179-80°. Hence, the above di-acid should have the structure (XIV: $R=R_1=H$), the authentic specimen of which was prepared as follows:

A Stobbe condensation was carried out with 2-methyl*cyclo*hexanone and dimethyl succinate in presence of potassium *tert.*-butoxide to yield β-carbomethoxy-β-(2-methyl-*cyclo*hexenyl)-propionic acid (XV: R=H) in 71% yield (cf. Cook and Phillip, *J. Chem. Soc.*, 1948, 162). The latter on hydrolysis with concentrated hydrochloric acid furnished the lactonic monocarboxylic acid (V: R=Me; $R_1=H$; $R_2=CO_2H$), m.p. 107°. This lactonic acid was also synthesised by the condensation of ethyl 2-methyl*cyclo*hexylidene-1-cyanoacetate (II: R=Me; $R_1=H$) with ethyl bromoacetate, followed by hydrolysis with concentrated hydrochloric acid. The acid (V: R=Me; $R_1=H$; $R_2=CO_2H$) on pyrolysis at 250-60° yielded a neutral lactone (V: R=Me; $R_1=R_2=H$), which was also prepared by Bachmann and Raunio (*J. Amer. Chem. Soc.*, 1950, **72**, 2530). It might be pointed out that the acid (C) did not undergo decarboxylation under the same condition. The synthesis of the acid (V: R=Me; $R_1=H$; $R_2=CO_2H$) excluded the latter structure for the acid (C). The half-ester (XV: R=H) was esterified

with diazomethane to yield the di-ester (XV : R=Me) which on hydrogenation, followed by alkaline hydrolysis, furnished the dicarboxylic acid (XIV : $R=R_1=H$), identical with the acid obtained from (C). This ruled out the structures (X : R = Me ; $R_1=CO_2H$; $R_2=H$) and (V : R=Me ; $R_1=CO_2H$; $R_2=H$) for the parent lactonic acid (C). Moreover, the acid (V : R=Me ; $R_1=CO_2H$; $R_2=H$) was prepared by Bachmann and Raunio (*loc.cit.*). The structures (X : R = Me ; R_1 = H ; R_2 = CO_2H) and (VI : R=Me ; $R_1=R_2=H$) were also excluded by the observation that the afore-mentioned hydroxy-ester, obtained from the acid (C) on oxidation according to the method of Fieser (*ibid.*, 1953, **75**, 4386), did not furnish a keto-ester. The hydroxy-ester on hydrolysis yielded the same lactonic acid (C). Hence, out of the remaining two structures (XII and XIII), the structure (XII) is preferred, avoiding the δ-lactonic structure (XIII) for the acid (C).

The neutral trimethyl ester (IV : $R=R_2=Me$; $R_1=R_4=CO_2Me$; $R_3=H$) underwent the Dieckmann cyclisation with sodium methoxide under nitrogen atmosphere to yield dimethyl 8-methylhydrind-$\Delta^{3:9}$-en-1-one-2 : 3-dicarboxylate (VII : $R=R_1=CO_2Me$), λ_{max}^{alc} 220 mμ (log ε 3.81), in 53-59% yield. When treated with sodium dust the β-keto di-ester was also obtained, but only in 30-35% yield. The ultraviolet spectrum of the β-keto di-ester suggests (Ungnade and Ortega, *ibid.*, 1951, **73**, 1564) that the double bond is in αβ-position with respect to the carbomethoxyl group at C_3. It has been reported by Dieckmann (*Ber.*, 1922, **55**, 2470) that ethyl *cyclo*pentanone-2-carboxylate exists primarily in the form of the keto derivative (4.5% enol) whereas ethyl *cyclo*hexanone-2-carboxylate exists primarily as the enol (76%) ; in 95% ethanol the values for enolic forms are 5% and 57% respectively as shown by Prelog *et al.* (*Helv. Chim. Acta*, 1951, **34**, 1954). These observations definitely excluded the possibility of the above β-keto di-ester to exist in the enolic form (VIII) as the main component. The above β-keto di-ester on hydrolysis with concentrated hydrochloric acid yielded the keto-acid (IX : $R=CO_2H$). The double bond of this acid was assumed to migrate in the *cyclo*hexane ring because no ultraviolet absorption maximum in the region 215-220 mμ, characteristic for the αβ-unsaturated acids and esters (Ungnade and Ortega, *loc. cit.*), was observed. This phenomenon of double-bond migration from the five-membered ring to the six-membered one, when these are fused together, is in quite agreement with the observations of Brown *et al.* (*J. Amer. Chem. Soc.*, 1954, **76**, 467) and also that of Dieckmann (*loc.cit.*) as well as of Kon (*J. Chem. Soc.*, 1926, 2727, 3101). The afore-mentioned keto-acid (IX : $R=CO_2H$) could also be obtained independently from the tri-ester furnished by acid (B).

With the expectation that decarboxylation with base might have preserved the double bond in the *cyclo*pentane ring, attempts were made to eliminate the carbomethoxyl group from the β-keto di-ester with various concentrations of sodium hydroxide and also of barium hydroxide ; unfortunately the attempts resulted only in the resinous product. The pure keto-acid (IX : $R=CO_2H$) under the same conditions of hydrolysis was also converted into similar polymerised product.

During the acid hydrolysis of the β-keto di-ester (VII : $R=R_1=CO_2Me$) a neutral fraction, having no characteristic absorption in the ultraviolet for the αβ-unsaturated

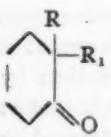
ketone, was obtained in extremely poor yield. This ketonic material on hydrogenation furnished a saturated ketone, the semicarbazone of which melted at 223° and the mixed melting point with the authentic semicarbazone of *cis*-8-methylhydrindanone-1 (XI: $R=R_1=H$) did not show any depression.

The unsaturated keto-acid, 3-carboxy-8-methylhydrind-$\Delta^{4:9}$-en-1-one (IX: $R=CO_2H$) on catalytic hydrogenation furnished the saturated keto-acid (XI: $R=H$; $R_1=CO_2H$). The latter compound on oxidation with concentrated nitric acid (Bagchi and Banerjee, this *Journal*, 1947, **24**, 12) yielded the known *cis*-1-methyl*cyclo*hexane-1 : 2-dicarboxylic acid, identified by comparison with an authentic sample prepared according to the method of Linstead and Millidge (*loc. cit.*).

The unsaturated keto-acid (IX : $R=CO_2H$) on pyrolysis was expected to eliminate carbon dioxide with the shift of the double bond to produce the unsaturated ketone (VII : $R=R_1=H$). This type of thermal decarboxylation was studied by Arnold *et al.* (*J. Amer. Chem. Soc.*, 1950, **72**, 4359) and also by Barton and Brooks (*J. Chem. Soc.*, 1951, 257). As the thermal decarboxylation of the unsaturated keto-acid (IX : $R=CO_2H$) could not be effected even at 390°-400°, it was heated with copper-bronze powder in quinoline to furnish the unsaturated ketone (VII : $R=R_1=H$ or IX : $R=H$) which on catalytic hydrogenation afforded *cis*-8-methylhydrindanone-1, identified through its semicarbazone (cf. Bachmann and Raunio, *loc. cit.*; Banerjee and Shafer, *J. Amer. Chem. Soc.*, 1950, **72**, 1931 ; Johnson, *ibid.*, 1944, **66**, 215 and references cited therein).

The trimethyl ester (IV : $R=R_2=Me$; $R_1=R_4=CO_2Me$; $R_3=H$) on hydrogenation by the Adams catalyst yielded the saturated trimethyl ester (XVII : $R=R_2=Me$; $R_1=R_3=CO_2Me$) which on the Dieckmann cyclisation, followed by the acid hydrolysis, furnished the saturated keto-acid (XI : $R=H$; $R_1=CO_2H$).

The double bond of the β-keto di-ester (VII : $R=R_1=CO_2Me$) is analogous to the $C_{14}-C_{15}$ ethylenic linkage of steroid and might be expected to produce a mixture of *cis* and *trans* compounds on hydrogenation (Johnson *et al.*, *ibid.*, 1947, **69**, 2942). But the above compound on catalytic hydrogenation, followed by hydrolysis, yielded the same saturated keto-acid (XI : $R = H$; $R_1 = CO_2H$), ring-fusion of which was conclusively proved to be *cis* by oxidation.



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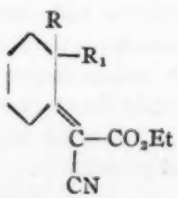

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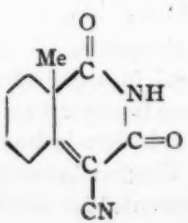

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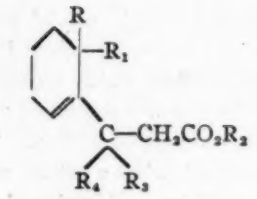

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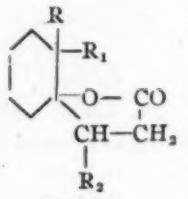

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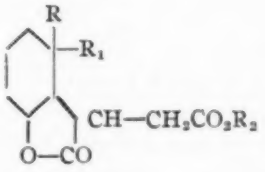

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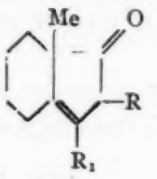

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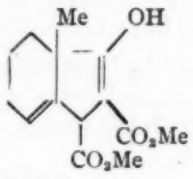

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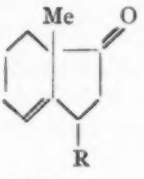

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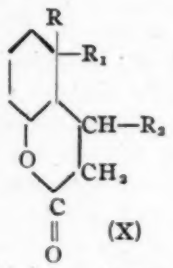

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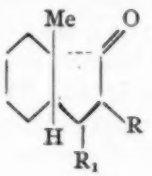

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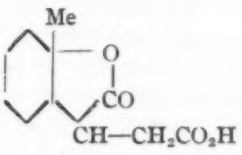

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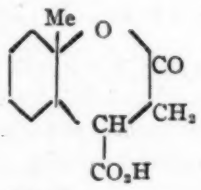

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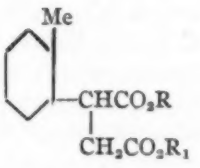

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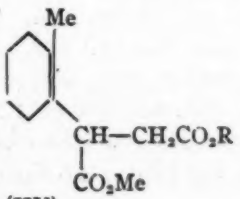

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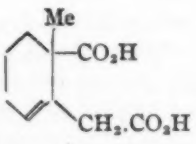

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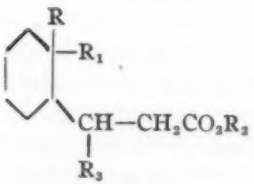

(XVII)

* EXPERIMENTAL

Ethyl 2-Methyl-2-carbethoxycyclohexylidene-1-cyanoacetate (II : R = Me ; $R_1 = CO_2Et$) *and Imide of 2-Methyl-2-carboxycyclohexylidene-1-cyanoacetic Acid* (III).—Ethyl cyano-

All m.p.s are uncorrected. The UV-spectrum was measured by the Unicum spectrophotometer SP. 500.

acetate (115 c.c.), ethyl 2-methyl*cyclo*hexanone-2-carboxylate (115 g.), glacial acetic acid (30 c.c.), ammonium acetate (12 g.) and dry benzene (250 c.c.) were refluxed in a flask, to which a water separator had been attached, until no further water separated. Further ammonium acetate (12 g.) was added and the refluxing was continued ; the process was repeated until the quantity of ammonium acetate amounted to 60 g. The mixture was refluxed for a total period of 30 hours. It was cooled, when a yellow solid (III), m.p. 226° (decomp.), separated out, yield 15 g. The solid was filtered and the crystalline mass was recrystallised 4 times from ethanol to furnish pure white crystals, m.p. 230-31° (decomp.) ; λ_{max}^{alc} 220mμ (log ε 4.026). (Found: C, 64.64; H, 6.15 ; N, 13.78. $C_{11}H_{12}O_2N_2$ requires C, 64.70 ; H, 5.88 ; N, 13.72%).

The dark brown filtrate was washed with water and the solvent was removed. Distillation of the residual oil gave a slightly viscous oil, b.p. 165-68°/1mm; η_D^{25} 1.4762, yield 107 g. (Lit. b.p. 160-65°/1mm).

*Diethyl α-Cyano-α-(2-methyl-2-carbethoxy*cyclo*hex - $\Delta^{1:6}$ - enyl) - succinate* (IV : R=Me; $R_1=R_4=CO_2Et$; R_2=Et; R_3=CN).—Sodium ethoxide, prepared from sodium (5.75 g.) and absolute ethanol (200 c.c.), was cooled to 0°-5° for 30 minutes. To it the above cyano-ester (70 g.) was added dropwise with constant shaking ; immediately the colour of the solution was changed to brown. The temperature of the alcoholic solution was maintained at 0°-5° for 1 hour more with frequent shaking. To this sodio-enolate ethyl bromoacetate (48 g.) was added all at a time and the reaction mixture was immediately refluxed on the water-bath for 16 hours. It was cooled, diluted with water and extracted 4 times with a mixture of ether and benzene. The extract was then washed twice with water. After removal of the solvent, a thick viscous oil was obtained, b.p. 195-200°/1mm, η_D^{25} 1.4780, yield 77.0 g. (Found : C, 62.34 ; H, 7.86. $C_{19}H_{27}O_6N$ requires C, 62.46 ; H, 7.39 %).

Hydrolysis of the above Succinate (IV : R=Me ; $R_1=R_4=CO_2Et$; R_2=Et ; R_3=CN).—(*a*). A mixture of the above succinate (58 g.) and HCl (conc., 650 c.c.) was heated under reflux for 36 hours. Most of the HCl was removed and after dilution with ice-cold water the organic acidic material was extracted thoroughly with ether. The ether extract was dried over anhydrous Na_2SO_4 and after removal of the solvent a viscous liquid was obtained. On attempting crystallisation from a mixture of ether and petroleum ether (b.p. 40-60°) a solid acid (8.0 g.), m.p. 130-45°, separated out. This acid was dissolved in a mixture of ethyl acetate (25 c.c.), dry ether (200 c.c.) and petroleum ether (50 c.c.) and the resulting solution was allowed to stand at room temperature for 7 days when the lactonic dicarboxylic acid (B), m.p. 182°, separated out ; yield 3.2 g. This was recrystallised 3 times from a mixture of ether and petroleum ether to afford the pure material, m.p. 184-85°. (Found : C, 56.01 ; H, 6.40 ; N.E., 130. $C_{12}H_{16}O_6$ requires C, 56.25 ; H, 6.25% ; N.E., 128).

From the mother-liquor the tricarboxylic acid (A), m.p. 148-50°, was obtained ; yield 6.8 g. Two further crystallisations from a mixture of ether and petroleum ether furnished the pure acid, m.p. 152-53°. (Found: C, 56.40 ; H, 6.45 ; N.E., 86. $C_{12}H_{16}O_6$ requiresC, 56.25 ; H, 6.25% ; N.E., 85.3).

(*b*). Again, when a mixture of the above succinate (38 g.) and HCl (conc., 600 c.c.) was heated under reflux for 55 hours and the hydrolysed product was extracted as before,

it yielded a viscous liquid. This was dissolved in a mixture of ether and petroleum ether (8 : 1) and the resulting solution was allowed to stand for 18 hours at room temperature when the lactonic monocarboxylic acid (C) crystallised out, m.p. 190-92°, yield 4.6 g. Four crystallisations from a mixture of ether and petroleum ether afforded the pure acid, m.p. 200°. (Found : C, 62.38 ; H, 7.15 ; N.E., 213. $C_{11}H_{16}O_4$ requires C, 62.27 ; H, 7.54% ; N.E., 212).

Esterification of the Crude Acids.—After removal of the solid lactonic acid (C), as stated above in (*b*), the remaining curde gummy acid mixture was esterified by refluxing with a mixture of dry methanol (250 c.c.) and H_2SO_4 (*d* 1.84, 35 c.c.) for 50 hours. The mixture was cooled and poured into crushed ice when a heavy oil separated out. It was repeatedly extracted with ether-benzene mixture. The extract was successively washed with water, ice-cold 5% NaOH solution and finally with water. The solvents were removed. Distillation of the residual oil furnished a yellow mobile liquid (IV : $R=R_2=Me$; $R_1=R_4=CO_2Me$; $R_3=H$), b.p. 155-60°/0.8 mm, η_D^{26} 1.4819, yield 29.5g. (Found : C, 60.50 ; H, 7.52. $C_{13}H_{22}O_6$ requires C, 60.39 ; H, 7.38 %).

The same ester was obtained from the acid (A) in excellent yield by means of diazomethane. Saponification of this ester with 20% methanolic KOH solution afforded the tricarboxylic acid (A).

The alkaline aqueous layer was acidified with HCl (dil.) and the precipitated oil was extracted with ether-benzene mixture to furnish the ester of the lactonic dicarboxylic acid (B), b.p. 160-62°/0.5 mm, yield 1.8 g. (Found : C, 59.18 ; H, 7.37. $C_{14}H_{20}O_6$ requires C, 59.15; H, 7.04 %). The same ester was obtained from the acid (B) by means of diazomethane. Hydrolysis of this ester with HCl (conc.) furnished the acid (B).

The methyl ester of the lactonic monocarboxylic acid (C) was prepared by treating the cold ethereal solution of the acid (C) (2.12 g.) with an ethereal solution of diazomethane, prepared from nitrosomethyl urea (1.8 g.) and allowing the reaction to proceed for 20 minutes. After decomposition of the excess of diazomethane with acetic acid, the reaction mixture was worked up as usual and evaporatively distilled at 140-45°/0.8 mm, yield 2 g. (Found : C, 64.12 ; H, 7.73 $C_{12}H_{18}O_4$ requires C, 63.71 ; H, 7.96%).

Interconversions of the Acids.—(*a*). A mixture of acid (A) (1 g.) and HCl (conc., 10 c.c.) was heated under reflux for 10 hours. Fresh HCl (conc., 10 c.c.) was added and the mixture was refluxed for another 10 hours. After working up as before, the residue was crystallised from dilute methanol to furnish the pure acid, m.p. 184-85°, yield 0.1 g. Mixed m.p. with the lactonic dicarboxylic acid (B), obtained before, was 183-84°.

(*b*). A mixture of the acid (A) (2 g.) and HCl (conc., 30 c.c.) was refluxed for 30 hours. After addition of fresh HCl (conc., 15 c.c.), the reaction mixture was further refluxed for 15 hours. After working up, the residue was crystallised thrice from a mixture of ether and petroleum ether to afford the pure acid, m.p. 200°, yield 0.026 g. On admixture with lactonic monocarboxylic acid (C), obtained before, the m.p. remained undepressed.

(*c*) Similarly, when a mixture of lactonic dicarboxylic acid (B) (2.5 g.) and HCl (conc., 40 c.c.) was heated under reflux for 30 hours, it yielded a gummy acid which on evaporative distillation at 150-60°/1 mm furnished the lactonic monocarboxylic acid, m.p. 199-200° ; yield 0.673 g. Mixed m.p. with the previous sample was 200°.

Dimethyl 8-Methylhydrind-$\Delta^{3:9}$-en-1-one-2 : 3-dicarboxylate (VII : R = R_1 = CO_2Me).—(*a*). To the sodium methoxide, prepared from sodium dust (1.57 g.) and methanol (2.8 c.c.) in dry benzene (30 c.c.), was added the neutral ester (10.3 g.) in dry benzene (40 c.c.). The mixture was then refluxed for 4-5 hours under nitrogen atmosphere. The solution was cooled under nitrogen and acidified with cold HCl (dil.). The organic layer was washed successively with water, ice-cold 5% aqueous KOH solution and finally with water. After removal of the solvent, the β-keto di-ester was distilled at 165-68°/1.5 mm ; η_D^{33} 1.4935, $\lambda_{max}^{alc.}$ 220 mμ (log ϵ 3.81), yield 5.30 g. (Found : C, 63.41 ; H, 6.40. $C_{14}H_{18}O_5$ requires C, 63.15 ; H, 6.76%).

(*b*). To a suspension of sodium dust (1.57 g.) in dry benzene (25 c.c.) was added a solution of trimethyl ester (10.03 g.) in dry benzene (40 c.c.) containing 5 drops of methanol. The mixture was then refluxed for 4 hours. The dark red solution containing solid suspension of the sodio-enolate was cooled and acidified with dilute hydrochloric acid. The β-keto di-ester, after working up as before, was distilled, yield 2.8 g.

3-Carboxy-8-methylhydrind-$\Delta^{4:9}$-en-1-one (IX : R = CO_2H).—(*a*). A mixture of the above β-keto di-ester (20.5 g.) and HCl (conc., 100 c.c.) was refluxed for 32 hours. The cooled solution, after dilution with ice-water, was repeatedly extracted with ether. The ethereal layer was then extracted 4 times with cold 5% aqueous NaOH solution, washed with water, dried over anhydrous Na_2SO_4 and after removal of the solvent a neutral ketone (0.28 g.), having strong camphoraceous odour and no characteristic absorption in the ultraviolet region for the $\alpha\beta$-unsaturated carbonyl grouping, was obtained.

The combined alkaline extract was acidified with HCl (dil.) and the precipitated oil was extracted several times with ether. After removal of the ether, the gummy keto-acid (10.2 g.) was crystallised from a mixture of ether and petroleum ether to afford the pure material, m.p. 160°. (Found : C, 68.45 ; H, 7.58 ; N.E., 196. $C_{11}H_{14}O_3$ requires C, 68.04 ; H, 7.21% ; N.E., 194).

The *semicarbazone* of the keto-acid, prepared by the pyridine method, after purification by crystallisation from dilute methanol, melted at 258° (decomp.). (Found : C, 57.20 ; H, 7.11. $C_{12}H_{17}O_3N_3$ requires C, 57.37 ; H, 6.77%).

(*b*). A solution of the β-keto di-ester (3.25 g.) in acetic acid (6 c.c.) and 6*N*-HCl (25 c.c.) was allowed to reflux for 16 hours. After working up as before, the residual gummy acidic material was evaporatively distilled at 110-15°/1.5 mm. The yellow semisolid distillate was crystallised as before, yielding the keto-acid (1.51 g.), m.p. 159-60°.

(*c*). A solution of the β-keto di-ester (1.85 g.) in a mixture of 48% HBr (6 c.c.), acetic acid (9 c.c.) and water (3 c.c.) was refluxed for 5 hours at 130° in an oil-bath. After removal of the acetic and hydrobromic acids the residual gummy material was worked up as before when the keto-acid (0.8 g.) was obtained as a thick oil which solidified completely after 4 days. Two crystallisations afforded a pure material, m.p. 159-60°.

(*d*). *From Lactonic Dicarboxylic Acid* (*B*).—To the solution of sodium (0.23 g.), dissolved in dry methanol (5 c.c.), was added a solution of the lactonic dicarboxylic acid (B) (1.15 g.) in methanol (5 c.c.) and the mixture was refluxed for 2 hours on a

water-bath, cooled and then treated in the cold with methyl iodide (5 c.c.). The reaction mixture was refluxed for 6 hours. Most of the methanol was distilled and the resulting liquid was poured into ice-water containing HCl (conc., 5 c.c.). The precipitated oil was extracted five times with ether. The combined ether extract was washed successively with ice-water, cold 5% aqueous NaOH solution (15 c.c.) and finally with water. After removal of the solvent, a neutral ester was obtained as a mobile yellow liquid, b.p. 155°/0.8 mm, η_D^{28} 1.4810, yield 0.83 g. (Found: C, 59.81; H, 7.63. $C_{13}H_{22}O_5$ requires C, 60.39; H, 7.38%). The neutral tri-ester on the Dieckmann cyclisation with sodium methoxide, followed by acid hydrolysis, yielded the same unsaturated keto-acid, m.p. 160°, as obtained above.

3-Carbomethoxy-8-methylhydrind-$\Delta^{4:9}$-en-1-one (IX: R = CO_2Me).—The methyl ester of the above keto-acid was prepared by treating the cold ethereal solution of the keto-acid (2 g.) with an ethereal solution of diazomethane, prepared from nitrosomethyl urea (2 g.) and allowing the reaction to proceed for 15 minutes. After working up as usual, the residue was evaporatively distilled at 120-25°/1.5 mm, yield 1.7 g. (Found: C, 68.95; H, 7.94. $C_{12}H_{16}O_3$ requires C, 69.23; H, 7.69%).

The *semicarbazone*, prepared by the pyridine method, was crystallised from dilute methanol, m.p. 220° (decomp.). (Found: C, 59.22; H, 7.38. $C_{13}H_{19}O_3N_3$ requires C, 58.87; H, 7.17%).

Methyl β-Carbomethoxy-(β-2-methyl-2-carbomethoxycyclohexyl)-propionate (XVII: R = R_2 = Me; R_1 = R_3 = CO_2Me).—To a suspension of pre-reduced PtO_2 catalyst (0.13 g.) in glacial acetic acid (15 c.c.) was added a solution of the unsaturated tri-ester (8 g.) in glacial acetic acid (15 c.c.) in an atmosphere of hydrogen. The theoretical amount of hydrogen (650 c.c.) was absorbed in 56 hours. After working up as usual, the residual oil on distillation gave a colorless mobile liquid, b. p. 155-57°/1 mm, η_D^{28} 1.4715, yield 7.8 g. (Found: C, 60.23; H, 8.41. $C_{15}H_{24}O_6$ requires C, 60.0; H, 8.0%).

cis-*Dimethyl 8-Methylhydrindan-1-one-2:3-dicarboxylate* (XI: R = R_1 = CO_2Me).—To the sodium methoxide, prepared from sodium dust (0.8 g.) and methanol (1.3 c.c.) in dry benzene (200 c.c.), was added a solution of the above saturated tri-ester (7.8 g.) in dry benzene (20 c.c.). The mixture was refluxed under nitrogen atmosphere for 4 hours. After working up as before, the residual liquid on distillation yielded a colorless oil, b.p. 135-40°/0.5 mm, yield 4.0 g. (Found: C, 62.50; H, 7.50. $C_{14}H_{20}O_5$ requires C, 62.69; H, 7.46%).

cis-*8-Methylhydrindan-1-one-3-carboxylic Acid* (XI: R = H; R_1 = CO_2H).—(*a*). To a pre-reduced suspension of PtO_2 catalyst (0.05 g.) in glacial acetic acid (10 c.c.) was added a solution of the unsaturated keto-acid (0.5 g.), m.p. 160°, in glacial acetic acid (10 c.c.) in an atmosphere of hydrogen. The theoretical amount of hydrogen (50 c.c.) was absorbed within 2 hours. Then it was filtered and most of the acetic acid was distilled under reduced pressure. The residue was cooled, diluted with ice-water and extracted 4 times with ether. The ether extract was dried over anhydrous Na_2SO_4 and distilled. The gummy acid on keeping in the refrigerator solidified. Three crystallisations from a mixture of ether and petroleum ether afforded

the pure material, m.p. 155-56° yield 0.4 g. (Found : C, 67.38 ; H, 8.22. $C_{11}H_{16}O_3$ requires C, 67.34 ; H, 8.16%). The keto-acid (IX : R = CO_2H) and its ester, however, could not be reduced by 10% Pd-C in alcoholic solution.

(*b*). A mixture of the above saturated β-keto di-ester (XI : R = R_1 = CO_2Me; 3.5 g.) and HCl (conc., 35 c.c.) was refluxed for 20 hours. On working up as before, the residue was evaporatively distilled at 110-15°/1 mm, yield 2.0 g. The semisolid distillate was crystallised thrice from a mixture of ether and petroleum ether to afford the pure material, m.p. 153-54°. The m.p. was undepressed on admixture of the same acid obtained before.

(*c*). To a suspension of 10% Pd-C (0.5 g.) in 95% ethanol (10 c.c.) was added a solution of the dimethyl 8-methylhydrind-$\Delta^{3:9}$-en-1-one-2 : 3-dicarboxylate (2 g.) in 95% ethanol (10 c.c.) in an atmosphere of hydrogen. The theoretical amount of hydrogen (170 c.c.) was absorbed within 5 hours. Then it was filtered and worked up as before. Distillation gave a colorless oil, b.p. 135-40°/0.6 mm, yield 1.8 g. This on hydrolysis with HCl (conc.) for 20 hours yielded the same saturated keto-acid, m.p. 153°.

Methyl cis-8-*Methylhydrindan-1-one-3-carboxylate* (XI : R = H ; R_1 = CO_2Me).—The above saturated keto-acid (1 g.) was esterified with diazomethane in cold ethereal solution. After working up as before, the residual oil was evaporatively distilled at 120°/0.9 mm, yield 0.8 g. (Found : C, 68.37 ; H, 8.64. $C_{12}H_{18}O_3$ requires C, 68.57 ; H, 8.57%).

The *semicarbazone*, prepared and purified as before, melted at 192-93°. (Found : C, 58.3 ; H, 8.0. $C_{13}H_{21}O_3N_3$ requires C, 58.42 ; H, 7.86%).

cis-1-*Methylcyclohexane*-1 : 2-*dicarboxylic Acid*.—The keto-acid (XI : R = H ; R_1 = CO_2H ; 1.38 g.) was heated with nitric acid (*d* 1.4, 9 c.c.) on a boiling water-bath for 1 hour. It was then refluxed with addition of water (8 c.c.) for further 1½ hours. The solution was evaporated as much as possible (about 10 c.c.) on the water-bath and then left in an evacuated desiccator containing solid KOH when the dicarboxylic acid (0.3 g.) separated out, m.p. 153°. It was thrice recrystallised from a mixture of ether and petroleum ether when the pure acid, m.p. 160°, was obtained. (Found : C, 57.86 ; H, 7.60. Calc. for $C_9H_{14}O_4$: C, 58.06 ; H, 7.52%).

cis-8-*Methylhydrindanone*-1 (XI : R=R_1=H).—(*a*). To a suspension of 10% Pd-C (0.05 g.) in 95% ethanol (10 c.c.) was added a solution of the unsaturated neutral ketone (0.27 g.), obtained from the hydrolysis of the β-keto di-ester, in 95% ethanol (10 c.c.) in an atmosphere of hydrogen. The uptake of hydrogen (40 c.c.) was very fast. It was filtered and the filtrate was concentrated. To this concentrated solution was added semicarbazide hydrochloride (0.3 g.) and pyridine (0.5 c.c.) and the mixture was refluxed for 5 minutes. After cooling, the alcoholic solution was diluted with water when white crystals of the semicarbazone (0.2 g.) of *cis*-8-methylhydrindanone-1, m.p. 195-200°, was obtained ; three crystallisations from dilute methanol afforded pure semicarbazone, m.p. 223° (bath temp. 200°). The mixed m.p. with the authentic sample was 222-23° (bath temp. 200°). (Found : C, 63.02 ; H, 9.02 ; N, 19.42. Calc. for $C_{11}H_{19}ON_3$: C, 63.15 ; H, 9.09 ; N, 20.09%).

(*b*). A mixture of 3-carboxy-8-methylhydrind-$\Delta^{4:9}$-en-1-one (0.8 g.), m.p. 156-57°, copper-bronze powder (0.1 g.) and dry quinoline (5 c.c.) was heated under reflux in an oil-bath (bath temp. 250°-270°) for 13 hours. The mixture was cooled, diluted with ether (50 c.c.) and filtered. The filtrate was washed successively with 6*N*-HCl (20 c c.), sodium bicarbonate solution and finally with water. The neutral fraction, evaporatively distilled at 100-105°/25 mm, was hydrogenated with 10% Pd-C catalyst (0.1 g.) in 95% ethanol (20 c.c.). The uptake of hydrogen (42 c.c.) was very fast. After filtration, the solution was concentrated and the ketone was converted into semicarbazone, m.p. 223°. The mixed m.p. with the authentic sample was 223° (bath temp. 200°).

(*c*). A mixture of the unsaturated keto-acid (1.2 g.), m.p. 160°, pyridine (6 c.c.) and HCl (conc., 24 c.c.) was heated under reflux for 2 hours according to the method of Johnson *et al.* (*J. Amer. Chem. Soc.*, 1947, **69**, 2942). No decarboxylation was effected and the original acid was recovered.

(*d*). The unsaturated keto-acid, m.p. 160°, was heated at 255°-270° and 390°-400° respectively for 24 hours without isolation of the expected unsaturated ketone, but some unchanged material could be recovered.

β-Carbomethoxy-β-(2-methylcyclohexenyl)-propionic Acid (XV: R=H).—To an ice-cold solution of potassium *tert.*-butoxide, prepared from potassium (4.3 g.) and dry *tert.*-butyl alcohol (100 c.c.), was added a mixture of 2-methyl*cyclo*hexanone (11.2 g.) and dimethyl succinate (22 g.) in *tert.*-butyl alcohol (20 c.c.) with constant shaking. The brownish red solution was heated under reflux for 60 minutes in an atmosphere of nitrogen and then kept at room temperature for 4 hours. Acidification with ice-cold 6*N*-HCl afforded a straw-yellow solution which was concentrated under reduced pressure. Sufficient water was added to the cold solution which was extracted 4 times with ether-benzene mixture. The solvent layer was thoroughly extracted with saturated sodium bicarbonate solution and the bicarbonate solution after acidification with cold dilute hydrochloric acid was extracted 5 times with ether-benzene mixture. After removal of the solvent, the half-ester was distilled, b.p. 145-50°/0.5 mm, yield 15.8 g. (Found: C, 64.00; H, 7.82. $C_{12}H_{18}O_4$ requires C, 63.71; H, 7.96%).

α-*(2-Methylcyclohexyl)-succinic Acid* (XIV: R=R$_1$=H).—(*a*). The half-ester (4.3 g.) was esterified with diazomethane in cold ethereal solution. After decomposition of the excess of diazomethane, the methyl ester, worked up as before, was distilled, b.p. 125-27°/4 mm, yield 3.6 g. This di-ester (3.6 g.) was reduced in glacial acetic acid (25 c.c.) in presence of platinum oxide (0.2 g.). The theoretical amount of hydrogen (350 c.c.) was absorbed within 7 hours. It was filtered, worked up as before, and distilled, b.p. 125-26°/4 mm, yield 2.95 g. Saponification of the above saturated di-ester (1.2 g.) was effected with 10% methanolic NaOH solution (20 c.c.). After 6 hours' refluxing methanol was removed completely. The residue after dilution with ice-water was acidified and the precipitated oil was repeatedly extracted with ether. The ether extract was washed once with saturated brine solution and dried over anhydrous Na_2SO_4. After removal of the solvent, the acid (0.95 g.), m.p. 134-38°, containing adhering gum, was crystallised thrice from a mixture of ether and petroleum

ether to afford pure acid, m.p. 155°. The mixed m.p. of this acid with that of the dicarboxylic acid obtained from the lactonic monocarboxylic acid (*c*) did not show any depression. (Found : C, 61.91 ; H, 8.00. $C_{11}H_{18}O_4$ requires C, 61.68 ; H, 8.41%).

(*b*). *From the Lactonic Monocarboxylic Acid* (*C*).—To the solution of sodium methoxide, prepared from sodium (0.092 g.) and methanol (4 c.c.), was added a solution of lactonic monocarboxylic acid (C : 0.424 g.), m.p. 200°, in dry methanol (14 c.c.). The reaction mixture was refluxed on the water-bath for 2 hours, cooled and then methyl iodide (2 c.c.) was added to it. It was allowed to reflux for 6 hours. After removal of methanol, the residue was diluted with water and worked up as described in previous experiment. After removal of the solvent, the hydroxy-ester was evaporatively distilled at 110-12°/0.2–0.3 mm, yield 0.45 g. (Found : C, 60.17 ; H, 8.74. $C_{13}H_{22}O_5$ requires C, 60.46 ; H, 8.53%). To a solution of the hydroxy-ester (0.5 g.) in glacial acetic acid (10 c.c.) was added a solution of sodium dichromate (1.5 g.) in glacial acetic acid (15 c.c.) and dry benzene (15 c.c.). The mixture was allowed to stand for 24 hours and then worked up as usual, but no keto-ester was obtained. The hydroxy-ester on hydrolysis with 10% methanolic NaOH solution, followed by acidification, yielded the same lactonic acid, m.p. 199-200°. An intimate mixture of the hydroxy-ester (0.45 g.) and fused potassium hydrogen sulphate (1.5 g.), taken in a sublimation tube, was introduced into the air chamber, previously heated to 180° and kept at that temperature for 1 hour under nitrogen. The dehydrated product was allowed to evaporatively distil at 80°-100°/0.1 mm. The sublimate was taken up in ether and the ethereal layer was washed successively with ice-water, ice-cold 5% aqueous NaOH solution and ice-water, and then dried over anhydrous Na_2SO_4. After removal of the ether, the unsaturated di-ester was evaporatively distilled at 90°-100°/0.2 mm, yield 0.27 g. (Found : C, 64.80 ; H, 7.89. $C_{13}H_{20}O_4$ requires C, 65.00 ; H, 8.33%).

To a suspension of pre-reduced PtO_2 catalyst (0.1 g.) in glacial acetic acid (10 c.c.) was added a solution of the above unsaturated di-ester (1.6 g.) in glacial acetic acid (15 c.c.) in an atmosphere of hydrogen. The theoretical amount of hydrogen (150 c.c.) was absorbed within 3 hours. Then it was filtered from the catalyst and worked up as before. The saturated di-ester was evaporatively distilled at 110-15°/0.4 mm, yield 1.25. (Found : C, 64.35 ; H, 9.10. $C_{13}H_{22}O_4$ requires C, 64.46 ; H, 9.09%).

A mixture of the above di-ester (1.18 g.) and HCl (conc., 12 c.c.) was refluxed for 8 hours. It was diluted with ice-water and worked up as before. The residue, after four crystallisations from a mixture of ether and petroleum ether, afforded the pure acid, m.p. 155-56°, yield 0.6 g. (Found : C, 61.34 ; H, 8.21. $C_{11}H_{18}O_4$ requires C, 61.68 ; H, 8.41%).

Diethyl α-Cyano-α-(2-methylcyclohex-$\Delta^{1:6}$*-enyl)-succinate* (IV: R=Me ; R_1=H ; R_2=Et ; R_3=CO_2Et ; R_4=CN).—To the cold solution of sodium ethoxide, prepared from sodium (2.3 g.) in absolute ethanol (100 c.c.), was added ethyl 2-methyl*cyclo*hexylidene-1-cyanoacetate (II : R=Me ; R_1=H ; 19.4 g.) dropwise with shaking under the conditions described before. Ethyl bromoacetate (17 g.) was added all at a time and refluxed on a water-bath for 8-10 hours. The reaction mixture was cooled and

after dilution with water the material was worked up as before. After removal of the solvent, the succinic ester was distilled, b.p. 168-75°/1 mm, η_D^{25} 1.4740, yield 17.6 g. (Found : C, 65.68 ; H, 8.16. $C_{16}H_{22}O_4N$ requires C, 65.48 ; H, 7.90%).

γ-(2-*Methylcyclohexyl*-β-*carboxy*-*spirobutyrolactone* (V : R=Me ; R_1 = H; R_2 = CO_2H).—(*a*). A mixture of the above succinate (6.8 g.) and HCl (conc., 125 c.c.) was heated under reflux for 16 hours. The resulting mixture was diluted with water and after saturation with common salt the acidic layer was extracted with ether. Ether extract was washed with brine solution and dried. After removal of the solvent the crude solid acid, m.p 98-101°, containing adhering gum, was obtained ; yield 2.1 g. Three crystallisations from a mixture of ether and petroleum ether afforded the pure acid, m.p. 107°. (Found : C, 62.07 ; H, 7.64 ; N.E., 21.4. $C_{11}H_{16}O_4$ requires C, 62.27 ; H, 75% ; N.E., 212).

(*b*). A mixture of the above half-ester (XV : R=H ; 2.3 g.) and HCl (conc., 20 c.c.) was heated under reflux for 24 hours. On evaporation of HCl the crude lactonic acid (2 g.), m.p. 104-105°, was crystallised twice from a mixture of ether and petroleum ether to afford the pure acid, m.p. 107°.

γ-(2-*Methylcyclohexyl*)-*spirobutyrolactone* (V : R=Me ; R_1=R_2=H).—An intimate mixture of the solid lactonic acid (2.55 g.) and powdered glass (3 g.), taken in a 25 c.c. Vigreux column Claisen flask, was heated in a metal bath at 240°-250° and kept at that temperature for 80 minutes, when there was practically no evidence of any reaction. It was distilled, b.p. 130-35°/4 mm, yield 1.73 g. The above lactone was taken up in ether which was successively washed with water, sodium bicarbonate solution and finally with water. After removal of the solvent, the residue was distilled, yield 1.60 g. (Found : C, 71.22 ; H, 9.01. Calc. for $C_{10}H_{16}O_2$: C, 71.44 ; H, 9.52%).

2-*Methyl*-2-*carboxycyclohex*-$\Delta^{1:6}$-*enyl*-1-*acetic Acid* (XVI).—A mixture of the imide of 2-methyl-2-carboxy*cyclo*hexylidene-1-cyanoacetic acid (III : 1.1 g.) and 20% aqueous NaOH (20 c.c.) was heated under reflux for 56 hours when the evolution of ammonia had completely ceased. On acidification the dicarboxylic acid, m.p. 157-59°, separated out, yield 0.43 g. Three crystallisations from a mixture of ether and petroleum ether afforded the pure acid, m.p. 169°. (Found : C, 60.50 ; H, 7.24. Calc. for $C_{10}H_{14}O_4$: C, 60.60 ; H, 7.07%). Mixed m.p. with the authentic sample of the acid, prepared as follows, was 169-70°.

Ethyl 2-methyl-2-carbethoxy*cyclo*hexylidene-1-cyanoacetate (1 g.) was refluxed with HCl (conc., 20 c.c.) for 24 hours. The acid was worked up with ether as before and on recrystallisation for 4 times from a mixture of ether and petroleum ether furnished the pure acid, m.p. 169-70°.

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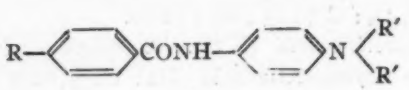
SEARCH FOR NEW LOCAL ANAESTHETICS. PART IV

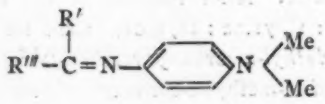
By I. Sen Gupta, (Miss) Harwant Kaur and Vasudev

Several basic anilides have been synthesised for studying their local anaesthetic activity.

Meyer (*Arch. exper. Path. Pharmakol.*, 1899, **42**, 109 ; 1901, **46**, 338) and Overton (*Arch. ges. Physiol.*, 1902, **92**, 115) observed that the potency of a local anaesthetic was due to its increased affinity for lipoids. Basic esters, in which the methylene group of the alkylene chain is replaced by a phenylene residue, have been studied by Fellows (*Proc. Soc. Exptl. Biol. Med.*, 1943, **53**, 7 ; *Chem. Abs.*, 1943 **37**, 4472), and some of these esters show good local anaesthetic activity. In the present investigation compounds of the general types (I) and (II) have been synthesised, where the alkylene chain connecting lypolitic and hydrophllic moieties has been replaced by a phenylene unit. It is expected that in these compounds the phenylene radical may further anchor the lypolitic moiety. The methoxy and the amino groups (I : R = OMe- and NH_2) *para* to the anaesthesiophoric group have been substituted in view of such groups being present in some known local anaesthetics.



(I)



(II)

In compounds of the general type (II) the >C=N- group is a polarised group similar to carbonyl group, and further these compounds possess also the necessary structural requirements of a local anaesthetic.

Compounds of the type (I) were obtained by treating *p*-dialkylaminoaniline with an acid chloride (anisic, *p*-toluic and *p*-nitrobenzoic). The nitro compounds were reduced to the corresponding amino derivatives. All the bases were smoothly converted into their hydrochlorides. For the preparation of compounds of the type (II) *p*-dimethylaminoaniline was refluxed with the carbonyl compound (piperonal, vanillin, anisaldehyde, acetophenone and salicylaldehyde) in alcoholic solution. The condensed products were converted into their hydrochlorides.

Experimental

(1). p-*Toluamido-4-dimethylaniline.*—*p*-Aminodimethylaniline (2.7 g., 0.02*M*) in dry ether (15 c.c.) was treated with *p*-toluoyl chloride (3.7 g., 0.024 *M*) in dry ether

(15 c.c.). The mixture was heated under reflux for 1 hour and the ether distilled off. The residue was treated with sodium bicarbonate solution. The product was collected, washed with water and crystallised from 90% alcohol in needles, m.p. 250°. (Found: N, 10.9. $C_{16}H_{18}ON_2$ requires N, 11.02%).

The *hydrochloride* of the base was prepared by saturating the solution of the base in absolute alcohol with dry HCl gas. Alcohol was distilled off and the residue crystallised from absolute alcohol, m.p. 262° (decomp.). (Found: N, 9.41. $C_{16}H_{19}ON_2Cl$ requires N, 9.64%).

(2). p-*Nitrobenzamido-4-dimethylaniline*.—*p*-Aminodimethylaniline (2.7 g., 0.02 *M*) was similarly treated with *p*-nitrobenzoyl chloride (4.5 g., 0.024 *M*) in ether solution. The nitro compound was crystallised from methyl alcohol in bronze needles, m.p. 257° (cf. Heilbron, "Dictionary of Organic Compounds", 1946, Vol. I, p. 75).

(3). p-*Aminobenzamido-4-dimethylaniline*.—The above nitro compound (3 g.) was added to stannous chloride (10 g.), dissolved in HCl (15 c.c.). The mixture was heated on a water-bath at 80-90° for 5 hours with occasional shaking. The mixture was cooled and treated with 65% NaOH solution (20 c.c.). The precipitated base was collected and washed with water. It was crystallised from dilute alcohol (charcoal) in needles, m.p. 179°.

The *hydrochloride* of the base was prepared in absolute alcohol. It could not be crystallised from any common solvent; however, it was washed thoroughly with dry acetone, absolute alcohol and dry ether, m.p. 252-53° (decomp.). (Found: N, 13.2. $C_{16}H_{17}ON_3.2HCl$ requires N, 12.8%).

Other analogous compounds in this series, prepared in a similar manner, are reported in Table I (No. 6 to 10).

(4). *4-Hydroxy-3 methoxybenzylidene-4-aminodimethylaniline*.—A mixture of vanillin (7.6 g.) and *p*-aminodimethylaniline (6.8 g.) in absolute alcohol (60 c.c.) was heated under reflux for 4 hours. Alcohol was partly distilled off when a solid product separated. It was cooled and the solid mass collected. A further amount of the product was also recovered from the filtrate. The compound was finally recrystallised from alcohol in needles, m.p. 138°.

The *hydrochloride* of the above base was prepared in dry ether and crystallised from absolute alcohol, m.p. 220°. (Found: N, 7.99; Cl, 20.6. $C_{16}H_{18}O_2N_2.2HCl$ requires N, 8.1; Cl, 20.7%).

(5). *2'-Hydroxybenzylidene-4-aminodimethylaniline* was similarly prepared by refluxing salicylaldehyde (6.1 g.) with *p*-aminodimethylaniline (6.8 g.) in absolute alcohol. The base came out to be a pasty mass and was therefore converted into its hydrochloride in dry ether, m.p. 171°. (Found: N, 8.8; Cl, 22.5. $C_{15}H_{17}ON_2.2HCl$ requires N, 8.9; Cl, 26.6%).

Other analogous compounds prepared in this series are reported in Table I (compounds No. 11 to 13).

TABLE I

[A stands for aniline.]

No.	Compounds.	Cryst. from	Melting points of the Compound.	Hydrochloride.	Mol. Formula.	Found.	Calc.
6.	*p*-Anisamido-4-dimethyl-A.	Abs. alcohol	176°	228° (dec.)	$C_{16}H_{18}O_2N_2$	N :10.50	10.37
7.	*p*-Nitrobenzamido-4-diethyl-A.	Dil. ,,	168°	...	$C_{17}H_{19}O_3N_3$	N :13.10	13.40
8.	*p*-Aminobenzamido-4-diethyl-A	,, ,,	206°	262° (dec.)	$C_{17}H_{21}ON_3$	N :14.68	14.84
9.	*p*-Toluamido-4-diethyl-A.	,, ,,	129°	245° (dec.)	$C_{18}H_{23}ON_3$	N :10.20	9.92
10	*p*-Anisamido-4-diethyl-A.	,, ,,	146°	234° (dec.)	$C_{18}H_{23}O_2N_3$	N : 9.01	9.39
11.	3′ :4′-Methylenedioxybenzylidene-4 aminodimethyl-A	,, ,,	112°	213°	$C_{16}H_{16}O_2N_2$	C :71.2 H : 5.8 N :10.4	71.6 5.9 10.4
12.	α-Phenylethylidene-4-aminodimethyl-A.	,, ,,	85°	168°	$C_{16}H_{18}N_2$	N :11.6	11.7
13.	4′-Methoxybenzylidene-4-aminodimethyl-A.	,, ,,	144°	242°	$C_{16}H_{18}ON_2$	N : 10.87	11.01

Compounds No. 3 and 6 have been tested at the Central Drug Research Institute, Lucknow for local anaesthetic activity. None of the compounds have any surface anaesthetic properties in 2% solution according to the method of Chance and Lobstein (*J. Pharmacol.*, 1944, **82**, 203). When tested for intradermal anaesthesia according to the method of Buibring and Wajda (*ibid.*, 1945, **85**, 78) in 2% solution in normal saline, the action started after one minute and lasted for 100 and 65 minutes respectively with inflammatory reaction. The compounds are being further studied for their pharmacological activity.

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ANALYTICAL ASPECTS OF SOME ORGANIC COMPOUNDS. PART VI. 2-HYDROXY-3-NAPHTHOIC ACIDS IN THE DETERMINATION OF THORIUM AND ZIRCONIUM

By Sachindra Kumar Datta

2-Hydroxy-3-naphthoic acid and its acetyl, bromo, iodo, nitro and nitroso derivatives have been used for the gravimetric determination of thorium and zirconium. Separation of thorium from the cerite earths and of thorium and zirconium from a number of foreign ions have been carried out with the bromo, iodo, nitro and nitroso compounds. They may also be used for the extraction of thorium from monazite sands. A considerable amount of zirconium may be separated from a smaller quantity of thorium when present in a mixture. Separation of thorium from uranium with the bromo, iodo and nitro compounds have also been described.

In Part V of this series (Datta, this *Journal*, 1957, **34**, 238), the possibility of using 2-hydroxy-3-naphthoic acid and its various derivatives as analytical reagents for various cations has been discussed and the methods for the gravimetric estimation of cobalt with 1-nitroso-2-hydroxy-3-naphthoic acid have been described. This latter acid has also been successfully employed in the determination of palladium and uranium (*Z. anal. Chem.*, 1957, **155**, 16). In the present communication the comparative utility of 2-hydroxy-3-naphthoic acid and its bromo, iodo, nitro and nitroso derivatives in the determination of thorium and zirconium has been investigated. Among all the acids used, the bromo, iodo, nitro and nitroso compounds have been proved suitable. Separation of thorium and zirconium from various foreign ions has also been made possible.

Experimental

The 2-hydroxy-3-naphthoic acid (B.D.H. reagent grade) was repeatedly crystallised from alcohol. 4:6-Dinitro-, 1-bromo-, 1:6-di-iodo-, 1-nitroso-2-hydroxy-3-naphthoic acids and 2-acetyl-3-naphthoic acid were prepared and purified according to the methods described previously (Datta, *loc. cit.*). 1% Solutions of nitro and nitroso compounds were prepared in hot water. An 1% solution of nitroso compound was also prepared in acetic acid by dissolving 1 g. of the substance in 30 c.c. of glacial acetic acid with the aid of heat and then diluting it to 100 c.c. with water. 1% Solutions of the other reagents were prepared in alcohol (75%).

Stock solutions of thorium and zirconium nitrates (A.R., Merck) were prepared and estimated with 2:4-D (Datta and Banerjee, this *Journal*, 1954, **31**, 397) and benzilic acid (Venkatramaniah and Rao, *ibid.*, 1951, **28**, 257; Klingenberg and Mendel, *Anal. Chem.*, 1954, **26**, 754) respectively. Stock solutions of other metals (all reagent grades) were prepared from their nitrates or chlorides and the metal contents determined by standard methods.

Optimum Conditions for the Determination of Thorium and Zirconium

Influence of p_H.—In order to find out a suitable p_H range for the estimation of thorium and zirconium with these reagents, precipitations were carried out in boiling solutions having different acid concentrations. A quantity of ammonium acetate was added in most of the cases. p_H of the solutions was measured after each precipitation. The results have been expressed as ThO_2 and ZrO_2, obtained after ignition of the precipitate, in Table I and Table II respectively. It appears from these tables that zirconium is precipitated from solutions at a lower p_H than thorium with the same reagent.

TABLE I

Precipitation of thorium at different p_H.

ThO_2 taken = 0.0216. g.

(-N indicates-3-naphthoic acid)

No. of reagent.	Reagent.	ThO_2 (in g.) found at p_H				
		2.6.	3.3.	3.8.	4.3.	5.3.
R_1	2-OH-N	0.0101	0.0132	0.0193	0.0212	0.0213
R_2	1-Br-2-OH-N	0.0123	0.0156	0.0216	0.0217	0.0214
R_3	1 : 6-Di-I-OH-N	0.0128	0.0201	0.0214	0.0213	0.0212
R_4	2-Acetyl-N	0.0072	0.0150	0.0173	0.0217	0.0214
R_5	4 : 6-Di-NO_2-2OH-N	0.0130	0.0209	0.0212	0.0216	0.0217
R_6	1-NO-2 OH-N	0.0110	0.0131	0.0215	0.0214	0.0212

TABLE II

Precipitation of zirconium at different p_H.

ZrO_2 taken = 0.0360 g.

Reagent.	ZrO_2 (in g.) found at p_H				
	2.0.	3.1.	3.6.	4.1.	5.2.
R_1	0.0173	0.0293	0.0355	0.0357	0.0353
R_2	0.0191	0.0301	0.0354	0.0357	0.0357
R_3	0.0187	0.0354	0.0356	0.0359	0.0358
R_4	0.0105	0.0283	0.0356	0.0356	0.0350
R_5	0.0196	0.0354	0.0363	0.0361	0.0359
R_6	0.0355	0.0358	0.0364	0.0362	0.0357

Effect of Temperature.—These acids do not produce complete precipitation in the cold. The precipitate becomes colloidal on long boiling. Hence, precipitation should be carried out from solutions at a temperature, little below the boiling point. Best results were obtained at 80°.

Effect of Ammonium Acetate.—A small amount of ammonium acetate is necessary for the complete precipitation of thorium and zirconium with all the reagents excepting the nitro and the nitroso derivatives. An excess of ammonium acetate, however, inhibits complete precipitation.

The thorium or zirconium solution was neutralised to Congo red, 25 c.c. of the reagent solution added and the mixture heated to 80° with the subsequent addition of a definite quantity of a 2% solution of ammonium acetate. The effect of ammonium acetate in the precipitation of metals has been indicated in Table III.

TABLE III

ThO_2 taken = 0.0432 g. ZrO_2 taken = 0.0360 g. Total vol. = 50 c.c.

Reagent.	Am. acetate (2%) added (in c.c.).	ThO_2 found (in g.).	ZrO_2 found (in g.).
R_1	0.5; 1.5; 2.0	0.0418; 0.0426; 0.0424	0.0332; 0.0353; 0.0340
R_2	0.5; 1.2; 1.5	0.0426; 0.0428; 0.0424	0.0357; 0.0354; 0.0350
R_3	0.5; 0.8; 1.0	0.0434; 0.0429; 0.0428	0.0358; 0.0360; 0.0354
R_4	0.5; 1.0; 1.5	0.0420; 0.0426; 0.0430	0.0352; 0.0355; 0.0355
R_5	—; 0.5; 1.0	0.0430; 0.0432; 0.0426	0.0360; 0.0361; 0.0355
R_6	—; 0.5; 1.5	0.0434; 0.0433; 0.0425	0.0361; 0.0362; 0.0344

Analytical Procedure.—An aliquot quantity of thorium or zirconium solution, made neutral to Congo red, was heated to 80°. To this was added with stirring an 1% solution of the reagent, followed by 1 c.c. of a 2% ammonium acetate solution. In the case of nitro and nitroso compounds, an 1% solution in hot water was used, while other reagents were used in solutions of alcohol (75%). The mixture was further heated for 5 minutes on a boiling water-bath so that the precipitate became coarser and collected at the bottom of the beaker. 2-Hydroxy-3-naphthoic acid and its bromo and iodo compounds furnished yellow precipitates of thorium and zirconium; with acetyl compound the colour of the precipitates was white, while the nitro and nitroso compounds formed deep yellow precipitates. The precipitate was filtered, washed with hot water and then with alcohol. After drying at 110°, the precipitate was ignited to the oxide to a constant weight. Some of the representative results have been tabulated below. Of the six reagents used, only the bromo, iodo, nitro and nitroso derivatives are suitable for the determination of these metals, and up to 4 mg. of these metals may be estimated with nearest accuracy.

TABLE IV

Determination of thorium and zirconium.

	R_1.	R_2.	R_3.	R_4.	R_5.	R_6.
ThO_2 taken.			ThO_2 found.			
0.0432 g.	0.0427 g.	0.0428 g.	0.0433 g.	0.0429 g.	0.0433 g.	0.0435 g.
0.0216	0.0212	0.0214	0.0218	0.0212	0.0217	0.0218
0.0162	0.0157	0.0159	0.0162	0.0156	0.0161	0.0162
0.0041	0.0030	0.0038	0.0040	0.0033	0.0040	0.0041
ZrO_2 taken.			ZrO_2 found.			
0.0405 g.	0.0399	0.0413	0.0403	0.0398	0.0408	0.0407
0.0270	0.0256	0.0269	0.0272	0.0264	0.0271	0.0274
0.0180	0.0174	0.0180	0.0181	0.0176	0.0182	0.0183
0.0045	0.0036	0.0040	0.0041	0.0036	0.0042	0.0044

Attempted Separation of Thorium and Zirconium with 1-Nitroso-2-hydroxy-3-naphthoic Acid

Zirconium is precipitated at a lower p_H than thorium with 1-nitroso-2-hydroxy-3-naphthoic acid. It was observed from preliminary experiments that zirconium could be precipitated in presence of considerable quantities of acetic acid, and not the latter. Attempts were therefore made to separate thorium from zirconium in acetic acid solution.

The solution containing the two metals was nearly evaporated to dryness; to the residue was added a considerable amount of 3.5*N* acetic acid solution, diluted to about 40 c.c. with water, and precipitation was carried out as before with the reagent. The washed precipitate was dissolved in the minimum quantity of dilute nitric acid with the aid of heat; requisite amount of acetic acid was then added and precipitation repeated. The precipitate was washed, dried and ignited to ZrO_2 as usual. The combined filtrate was evaporated to a small volume; thorium was precipitated from it as hydroxide with ammonia and ignited to oxide. The presence of thorium, if any, in the zirconium precipitate was tested with 'SNANDS' reagents (Datta, *Z. anal. Chem.*, 1956, **149**, 270). The results recorded in Table V indicate that only a small amount of thorium, if present, can be removed from zirconium.

TABLE V

Separation of thorium from zirconium with 1-nitroso-2-hydroxy-3-naphthoic acid.

Metals taken.		3.5*N*-acetic acid	Metals found.	
ZrO_2.	ThO_2.	added.	ZrO_2.	ThO_2.
0.0270 g.	0.0162 g.	5 c.c.	0.0351 g.	...
0.0270	0.0162	10	0.0310	...
0.0270	0.0162	15	0.0293	0.0132 g.
0.0270	0.0162	20	0.0275	0.0158
0.0270	0.0162	25	0.0272	0.0160
0.0270	0.0216	30	0.0296	0.0193
0.0270	0.0216	40	0.0287	0.0198

Separation of Thorium from Rare-earth.

Separation of thorium from the cerite earths was carried out with the bromo, iodo, nitro and nitroso derivatives only; the other two were found unsuitable. The mixture was neutral to Congo red and thorium was precipitated and estimated as before. The results shown in Table VI reveal that bromo and iodo compounds may separate thorium from a mixture having thoria-earth oxide ratio = 1:15, the corresponding ratio for the nitro and nitroso compounds is 1:18. The slight contamination may easily be removed by double precipitation.

TABLE VI

ThO_2 taken = 0.0122 g.

CeO_2 added.	La_2O_3 added.	ThO_2 : RO.	ThO_2 found.	CeO_2 added.	La_2O_3 added.	ThO_2 : RO.	ThO_2 found.
	By R_2.				By R_3.		
0.0276 g.	...	1 : 2.3	0.0126 g.	0.1104 g.	0.0304 g.	1 : 11 5	0.0124 g.
0.0552	0.0304 g.	1 : 7	0.0127	0.1104	0.0912	1 : 16	0.0127
0.1104	0.0912	1 : 16	0.0129	0.1104	0.0988	1 : 17	0.0130
	By R_5.				By R_6.		
0.0552	0.0304	1 : 7	0.0123	0.1104	0.0380	1 : 12	0.0125
0.1104	0.0380	1 : 12	0.0125	0.1104	0.0912	1 : 16	0.0126
0.1104	0.1140	1 : 18	0.0127	0.1104	0.1140	1 : 18	0.0128

Separation of Thorium and Zirconium from Diverse Ions

Definite quantities of metal salt solutions were separately added to a fixed amount of thorium or zirconium solution. The p_H of the mixture containing thorium was brought to 3.8 and that containing zirconium to 3.5, by adding buffer solutions. The precipitations of thorium and zirconium were carried out as before with the bromo, iodo, nitro and nitroso compounds. It was found that these metals could be separated from a number of foreign ions, Cu, Cd, Bi, Ca, Ba, Sr, Zn, Mg, Cr, Mn, Ni and V. Pb^{II}. Hg^{I}, Hg^{II}, Fe^{II}, Fe^{III}, and Ce^{IV} interfere in the determination with all these reagents. Aluminium and titanium cause heavy interference with the nitro compound, while cobalt, palladium and uranium (Datta, *loc. cit.*) exhibit quantitative interference with the nitroso compound. The results have been indicated in Table VII.

TABLE VII

Metal oxide added.		ThO_2 taken = 0.0216 g. ThO_2 found by				ZrO_2 taken = 0.0180 g. ZrO_2 found by			
		R_2.	R_3.	R_5.	R_6.	R_2.	R_3.	R_5.	R_6.
CuO	0.0203 g.	0.0213 g.	0.0215 g.	0.0213 g.	0.0218 g.	0.0181 g.	0.0177 g.	0.0184 g.	0.0182 g.
CdO	0.0317	0.0212	0.0214	0.0218	0.0215	0.0182	0.0183	0.0180	0.0182
BiO	0.0281	0.0214	0.0217	0.0218	0.0216	0.0178	0.0182	0.0184	0.0183
CaO	0.0132	0.0213	0.0213	0 0215	0.0214	0.0180	0 0181	0.0179	0.0184
BaO	0.0250	0 0212	0.0215	0.0217	0.0216	0.0177	0.0178	0.0183	0.0181
SrO	0.0218	0.0215	0 0213	0.0218	0.0216	0.0182	0.0180	0.0184	0.0184
ZnO	0.0153	0.0213	0.0214	0.0213	0.0212	0.0181	0.0176	0.0180	0.0183
*Cr_2O_3	0.0232	0.0212	0.0214	0.0217	0.0219	0.0184	0.0183	0.0183	0.0182
MnO_2	0.0105	0.0212	0.0215	0.0214	0.0218	0.0176	0.0183	0.0179	0.0181
MgO	0.0139	0.0214	0.0216	0 0216	0.0218	0.0179	0.0184	0.0182	0.0183
V_2O_5	0.0131	0.0212	0.0213	0.0212	0.0213	0.0175	0.0177	0.0177	0.0183
*NiO	0.0266	0.0218	0.0217	0.0217	0.0216	0.0184	0.0184	0.0183	0.0184
*CoO	0.0167	0.0213	0.0214	0.0217	...	0.0182	0.0184	0.0184	...
PdO	0.0216	0.0211	0.0213	0.0218	...	0.0181	0.0183	0.0180	...
*Al_2O_3	0.0232	0.0212	0.0211	0.0213	0 0213	0.0185	0.0181	0.0184	0.0183
TiO_2	0 0252	0.0213	0.0212	...	0.0220	0 0178	0.0184	...	0.0185

Separation of Thorium from Uranium

The bromo, iodo and nitro derivatives of 2-hydroxy-3-naphthoic acid may also be used for the separation of thorium from a large amount of uranium. Thorium was therefore precipitated with the three reagents from mixtures containing different quantities of thorium and uranium by following the same procedure. It was observed that the bromo, iodo and nitro compounds may separate thorium from mixtures having thoria-uranium oxide ratio up to 1 : 17, 1 : 18 and 1 : 21 respectively by double precipitation method. The results are shown in Table VIII.

TABLE VIII

ThO_2 taken.	U_3O_8 added.	$ThO_2 : U_3O_8$.	ThO_2 found by R_2.	R_3.	R_5.
0.0122 g.	0.0424 g.	1 : 3.5	0.0125 g.	0.0123 g.	0.0123 g.
0.0122	0.1060	1 : 8.7	0.0126	0.0123	0.0124
0.0122	0.1696	1 : 13.5	0.0126	0.0125	0.0124
0.0122	0.2120	1 : 17.3	0.0127	0.0126	0.0125
0.0162	0.3074	1 : 18.3	0.0170	0.0167	0.0166
0.0162	0.3498	1 : 21.5	...	0.0170	0.0167
0.0162	0.3710	1 : 22.9	...	0.0174	0.0169

Extraction of Thorium from Monazite Sand

The four reagents, viz., the bromo, iodo, nitro and nitroso compounds of 2-hydroxy-2-naphthoic acid, were used for the extraction of thorium from monazite sand. The precipitation was carried out as before from the acid extract of the sands; the precipitate was washed several times with hot water in order to remove the adhering cerite earths completely and ignited to the oxide. Estimation with 2 : 4-D (Datta and Banerjee, *loc. cit.*) was also carried out side by side for comparison. The results are recorded in Table IX.

TABLE IX

Reagent.	Wt. of sample.	Wt. of ThO_2 obtd.	% Recovery of ThO_2.
R_2	1.3250 g.	0.0966 g.	7.29
	1.1232	0.0820	7.30
R_3	1.5031	0.1089	7.30
	1.3250	0.0968	7.31
R_5	1.3250	0.0970	7.32
	1.1232	0.0821	7.31
R_8	1.3250	0.0967	7.30
	1.1232	0.0822	7.32
2 : 4-D	1.1232	0.0821	7.31
	1.5031	0.1100	7.32

The author desires to express his thankfulness to Dr. S.C. Shome of the Presidency College, Calcutta, Dr. B. N. Bose, Principal of this college and Dr. S.K Sinha, for their keen interest in the work and helpful encouragements.

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COPE-KNOEVENAGEL REACTION DYNAMICS. PART II. THE ROLE OF ACETIC ACID AS THE IONISING MEDIUM

By C. R. Raha

In a condensation reaction of levulinic ester with cyanoacetic ester, the proportions of ammonium acetate and acetic acid have been varied. It is concluded that the function of acetic acid is limited not exclusively to a simple ionisation.

It has been mentioned in the preceding part (this *Journal*, 1953, **30**, 205) that acetic acid serves as the ionising medium and benzene is the best solvent for removal of water. Perhaps the function of the acetic acid is limited not only to a simple ionisation but something more which will be clear from the results obtained in the present investigation.

The results in Tables I to IV refer to the yields of the product of condensation of levulinic ester with cyanoacetic ester in presence of varying proportions of ammonium acetate, the catalyst and acetic acid. In all the experiments the proportions of the reactants, except the catalyst and acetic acid, and the conditions are as described in the Experimental.

Experimental

Equimolar amounts (0.1 *M*) of levulinic ester and cyanoacetic ester together with ammonium acetate and acetic acid in benzene (75 c.c.) were refluxed for 3 hours with varying amounts of the acid or the catalyst in the apparatus described previously (*loc. cit.*) to remove the water continuously as formed. The time was kept constant whether the reaction came to an end or not. Table I records the yield with varying quantities of acetic acid, keeping that of ammonium acetate constant at 0.025*M*. It will be seen that corresponding to 0.075-0.1 *M*, the yield is maximum. On either side of the maximum unchanged materials were recovered.

Table I

Acetic acid (*M*)	0	0.025	0.05	0.075	0.1	0.2	0.4
Yield (g.)	9.5	11.5	14.8	17.0	17.5	14.0	11.5

The yield data in a similar series of experiments in which the acetic acid was fixed at 0.1*M* and the proportion of ammonium acetate was varied from 0.025 to 0.4 *M* are shown in Table II.

Table II

Am. acetate (*M*)	0.0	0.025	0.05	0.1	0.2	0.4
Yield (g.)	0.0	17.18	15.5	14.4	13.3	9.8

The lower yield on either side of the maximum, however, is found unlike the preceding case to be due to the formation of high boiling or even solid byproducts.

A higher proportion of acetic acid generally favours a large yield as the data in Table III show. Of course, it should be admitted that with a variation of acid concentration there is some variation also of the catalytic constant (Bell and Lidwell, *J. Chem. Soc.*, 1939, 1096).

TABLE III

	Acetic acid.	Am. acetate.	Yield.
Case I	0.1 *M*	..025*M*	17.7 g.
	0.025	0.1	14.0
Case II	0.15	0.05	17.0
	0.05	0.15	13.1

But it is not only the proportion of the two, but the absolute quantities of the catalyst and the acetic acid are also to be taken into consideration to ensure higher yield. For instance, the results in Table IV were obtained with a constant proportion of the acid to the catalyst, but their net concentrations were gradually increased. The proportion corresponding to 0.1*M* Am. acetate and 0.15 *M* acetic acid appears to provide the maximum yield. However, all proportions were not tried and, hence, the optimum combination of the acid and the catalyst could not be obtained.

TABLE IV

Am. acetate (*M*)	....	0.025	0.050	0.075	0.1	0.2
Acetic acid (*M*)	...	0.0375	0.075	0.113	0.15	0.3
Yield (g.)	...	6.8	15.4	16.0	16.6	11.0

It is known that elimination of water at the last stage is catalysed by acid. That is possibly the reason why a larger quantity of acid ensures a higher yield.

Two other catalysts besides ammonium acetate were tried in another series of experiments, in which 0.1*M* acetic acid was used. The proportion of the remaining reactants and the experimental conditions were the same as before. It will be clear from Table V that ammonium acetate is undoubtedly the best catalyst studied so far.

TABLE V

Catalyst.	Yield.
0.025 *M* acetamide	1 g.
,, piperazine diacetate	12
,, Am. acetate	11.5

The net reaction

is a reversible one (Wittig and Hartmann, *Ber.*, 1939, **72**, 1387 ; Cope *et al.*, *J. Amer. Chem. Soc.*, 1941, **63**, 3452) and should consequently be catalysed by acetate ion.

Brönsted (*Chem. Rev.*, 1928, **49**, 2327) is of the opinion that almost all acid-base catalysed reactions take place through the preliminary formation of a critical complex which acts as a very reactive intermediate. Such an idea was also envisaged by Watson (*Ann. Rept. Chem. Soc.*, 1939, **36**, 214 ; cf. Bell and Caldin, *J. Chem. Soc.*, 1938, 382) for the Knoevenagel reaction. The formation of a critical complex is also supported by our experiments with different solvents described earlier (Raha, *loc. cit.*). There, it has been found that with donor solvents like Ac_2O, thioether etc., the unchanged materials are received back.

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TRANSPORT NUMBER OF LEAD AND CADMIUM IN THEIR NITRATES BY ANALYTICAL BOUNDARY METHOD

By D. Mangaraj and S. Aditya

The transport number of cadmium and of lead in their nitrate solutions have been determined by analytical boundary method over the concentration range of $0.01M - 0.5M$. In case of cadmium, with changes in concentration, the transport number decreases slowly (from 0.426 to 0.403) and in case of lead it shows an increase (0.40 to 0.49). The experimental results have been explained quantitatively in the light of interionic attraction and the incomplete dissociation of the intermediate ions.

In a previous communication (this *Journal*, 1953, **30**, 217) the transport number of cadmium in cadmium nitrate solution was determined by Hittorf's method. In the present investigation transport measurements have been made by analytical boundary method developed by Brady (*J. Amer. Chem. Soc.*, 1948, **70**, 911). Spiro and Patron (*Trans. Faraday Soc.*, 1952, **48**, 263) improved the experimental technique and determined the transport number of silver in silver nitrate at various concentrations using KNO_3 and $NaNO_3$ solutions as indicator solutions. Their results were correct to 7 in the fourth decimal place. This accuracy compares fairly well with those ordinarily obtained from moving boundary experiments and cannot be achieved by Hittorf's method.

Experimental

The apparatus was more or less the same as that used by Spiro and Patron (*loc. cit.*). They used an electronically controlled constant current source and checked the constancy of the current by means of a potentiometer. In this work, however, voltage was kept constant by means of a voltage regulator and the total electricity passed was measured by a silver coulometer, and in some cases by silver as well as iodine coulometers. The working of the apparatus was tested from time to time by determining the transport number of silver ion in silver nitrate solution.

Merck's analytical reagent lead nitrate and cadmium nitrate were used. Ferric nitrate was prepared by dissolving precipitated and washed $Fe(OH)_3$ in extra pure nitric acid. Extra pure lead and cadmium were used as anode.

Cadmium was determined either iodimetrically or sometimes gravimetrically with 8-hydroxyquinoline. Lead was estimated gravimetrically as lead chromate.

The concentration of the indicator solution was calculated by using Kohlrausch's relation. Transport number determinations were made with various concentrations of the indicator solutions, some higher and some lower than the Kohlrausch's concentration, and the transport values were found to be on the plateau region. Experiments were done in triplicate and the average values of the transport numbers and the deviations from the mean are indicated in Tables I and II.

The transport number of cadmium or lead has been calculated as the amount of the particular ion crossing the boundary in g. equiv./g. equiv. of silver deposited in the coulometer. The transport numbers, thus calculated, are shown in Tables I and II.

TABLE I

Cd *in cadmium nitrate soln.*

Conc.	Transport number.
0.01 *M*	0.426 ± 0.002
0.02	0.416 ± 0.003
0.05	0.413 ± 0.003
0.10	0.413 ± 0.003
0.20	0.406 ± 0.002
0.50	0.403 ± 0.003

TABLE II

Pb *in lead nitrate soln.*

Conc.	Transport number.
0.015 *M*	0.46 ± 0.01
0.02	0.46 ± 0.003
0.05	0.47 ± 0.007
0.10	0.48 ± 0.004
0.25	0.49 ± 0.01
0.50	0.49 ± 0.01

DISCUSSION

From the results it appears that the transport number of cadmium in cadmium nitrate solution decreases with concentration (Table I) whereas in the case of lead in nitrate (Table II), the transport number increases with concentration. It may give the impression that there might be some defect in the experimental technique. Analysis of the data according to the scheme, discussed in the subsequent section, shows that it is not so. This apparent anomaly is due to the difference in the association constants of the intermediate ion (MA^+) in the two cases.

According to the usual definition, the transport number of anion in an electrolyte solution is the fraction of the total current passed, carried by that ion. This rather is a too much simplified definition of the transport number. This can be determined only when an electrolyte is completely dissociated in solution (nomenclature and definition: McBain, "Colloid Science", pp. 253-55; Alberty, *J. Amer. Chem. Soc.*, 1950, **72**, 2361; Spiro, *J. Chem. Ed.*, 1956, **33**, 464). When an electrolyte is not completely dissociated, then what we measure (by the ratio amount of a particular ion crossing the boundary in g. equiv./g. equiv. of silver deposited in the coulometer) is the transport number of the ion constituent (Spiro, *loc. cit.*) which is defined by the equation

$$T_R = \left(\frac{z_R}{|z_R|}\right) = \frac{\Sigma U_i m_i . n_{R,i} \left(\frac{z_i}{|z_i|}\right)}{\Sigma U_i m_i |z_i|}$$

where T_R = transport number of the ion constituent R.

U_i = mobility of the species i.

m_i = molarity of the species i.

$n_{R,i}$ = number of g. equiv. of ion constituent R, in one g. formula wt. of species i.

z_i = algebraic equivalence per formula of the species i.

$|z_i| = + \sqrt{z_i^2}$.

$\frac{z_R}{|z_R|} = +1$ for cation species and -1 for anion species.

Lead nitrate and cadmium nitrate may not exist in solution in completely dissociated state. Assuming the first stage of dissociation to be complete, the second incomplete and using the symbol MA_2 for $Pb(NO_3)_2$ or $Cd(NO_3)_2$, the equilibrium may be represented as

$$\underset{(1-\alpha)m}{MA_2} \xrightarrow[\text{dissociation.}]{\text{Complete}} \underset{m}{MA^+} + A^-$$

$$\Downarrow$$

$$\underset{\alpha m}{M^{2+}} + \underset{\alpha m}{A^-}$$

The transport number of the ion constituent M^{2+} ($T^{MA_2}_{M^{2+}}$) is given by,

$$T^{MA_2}_{M^{2+}} = \frac{2\alpha\, mU_{M^{2+}} + 2\,(1-\alpha)mU_{MA^+}}{2\alpha\, mU_{M^{2+}} + (1-\alpha)mU_{MA^+} + (1+\alpha)mU_{A^-}}$$

where α is the degree of dissociation of MA^+ and m, the molarity of the solution with respect to MA_2.

To test this equation, one may calculate the $T^{MA_2}_{M^{2+}}$ from the equation and compare with the experimental values or using the experimental values calculate the dissociation constant and compare that with the value of the dissociation constant determined by other methods. This is difficult as U_{MA^+} cannot be determined directly.

The dissociation constants for $PbNO_3^+$, $CdNO_3^+$ have been reported from conductance measurements by Davies *et al.* (*Trans. Faraday Soc.*, 1930, **26**, 572). The value of the dissociation constant for $PbNO_3^+$ has also been recently obtained by Hershenson, Smith and Hume (*J. Amer. Chem. Soc.*, 1953, **75**, 507) and Bale, Davies and Monk (*Trans. Faraday Soc.*, 1956, **52**, 816) from spectrophotometric measurements. From these measurements one can get the value of α and take the value of U_{MA^+} either on the basis of Davies's assumption or nearly half that of $U_{Cd^{2+}}$ on an analogy between that of Cd^{2+} and CdI^+ (Alberty, *et al.*, *J. Amer. Chem. Soc.*, 1951, **73**, 517).

If $T^{MA_2}_{M^{2+}}$ is calculated on this basis, it is found that the transport number should increase with concentration. For example, in case of cadmium nitrate, transport number will be 0.4306 when $\alpha=1$ and about 0.55 when $\alpha=0$ (*i.e.* when the species in the solution are $CdNO_3^+$ and NO_3^-). Similar will be the case with lead nitrate.

If no intermediate ions were formed, the transport number would have decreased with concentration due to the interionic attraction as in the case of $Zn(ClO_4)_2$ (*J. Amer. Chem. Soc.*, 1946, **68**, 338) and barium chloride.

So in case of electrolytes of the type MA_2, where there are MA^+ ions, there will be two opposing factors affecting the value of the transport number: (i) interionic force which will tend to decrease the transport number with concentration, and (ii) partially dissociated intermediate ion which will lead to an increase in the value of the transport number with increase in concentration.

Therefore, depending on the magnitude of K (the dissociation constant) one or the other effect will be predominant or may balance. If K is large, the interionic effect

will be more, and there will be a decrease in the value of transport number with concentration. If K is such that the effect are comparable, then the transport number may decrease or increase with concentration depending on whichever factor is more effective. As pointed out earlier, only a semiquantitative analysis of the results is possible. It has also been mentioned earlier that since K for $PbNO_3^+$ is smaller than that for $CdNO_3^+$, there would be more $PbNO_3^+$ than $CdNO_3^+$ in respective solutions at the same concentration. So increase with reference to the standard, say transport number for $Zn(ClO_4)_2$ (assuming normal behaviour), the increase in $Pb(NO_3)_2$ will be more than that in $Cd(NO_3)_2$. That is what we find in analysing our results. These results thus may be taken to be indicating the presence of intermediate MA^+ ions. No attempts to calculate their equilibrium constant has been made as the accuracy is not high and uncertainty also lies about the mobility of MA^+.

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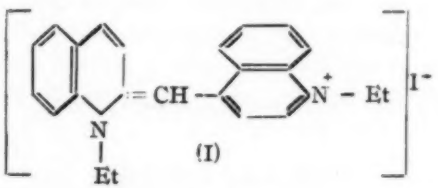
PHOTOGRAPHIC SENSITISERS. PART I. MEROCARBOCYANINES

By B. K. Patnaik and M. K. Rout

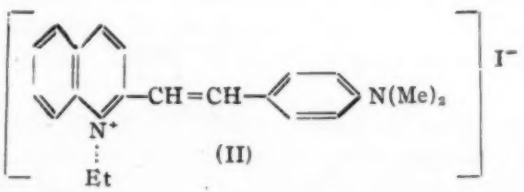
The preparation of five merocarbocyanine dyes derived from 4-phenyl-, 4-*p*-methoxyphenyl-, 4-*p*-ethoxyphenyl-, 4-*p*-bromophenyl-2-methylthiazoles and 2-methylbenzothiazole has been described. Their acetanilidovinyl intermediates were first prepared and then condensed with 3-ethyl-rhodanine to furnish the desired merocyanines,

Recently many dyes are being used in photography for modifying the spectral sensitivity of silver halide emulsions. The region of sensitivity conferred by the dye molecules is not confined to the visible spectrum, but extends to infra-red and even to longer wave-lengths. Because of the wide limits of sensitivity, thus provided, sensitising dyes have become indispensable in modern photography.

The dyes, which show the photographic sensitising action most powerfully, generally belong to the group known as the polymethine dyes which may be divided into three main divisions: the cyanines (I), *p*-dialkylaminostyryl dyes (II) and the merocyanines (III).



(I)



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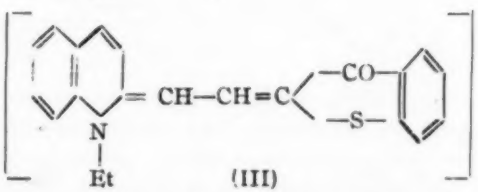
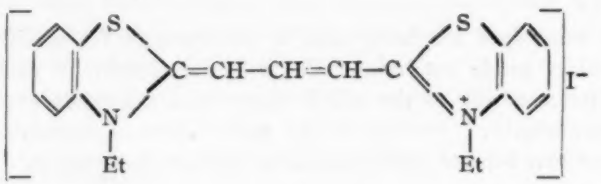


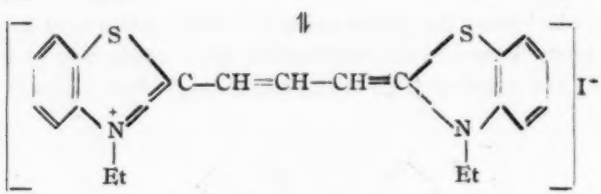
(III)

In the cyanine dyes, two basic nuclei are linked together, the two nitrogen atoms being separated by a conjugated chain of carbon atoms. In *p*-dialkylaminostyryl dyes, the conjugated chain exists, but one of the nitrogen atoms forms part of a

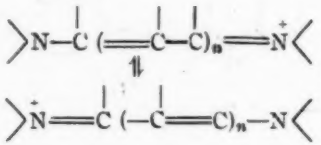
dialkylaminostyryl groups. These are much less important than cyanines. The third group of dyes, a more recent development, known as merocyanines, are as significant as cyanines. "Meros" means a portion. These are called merocyanines, since a part of the molecule resembles cyanines. The second half of the molecule is derived from an acidic rather than a basic nucleus. Unlike the other two classes, these dyes are unionised.

Whereas the cyanines are characterised by an amidinium ion resonance (IV), the merocyanine contains the amidic resonance system as shown in the simple forms in (V) or in a typical merocyanine dye (VI).

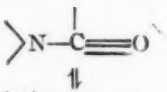




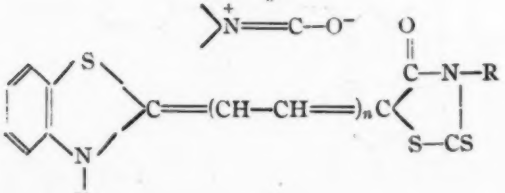
(IV)



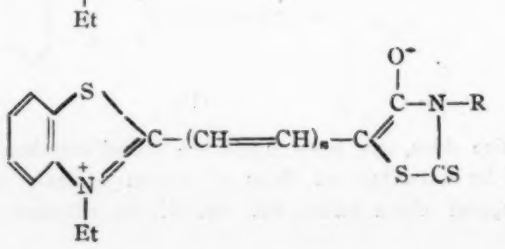
(V)



(VIa)

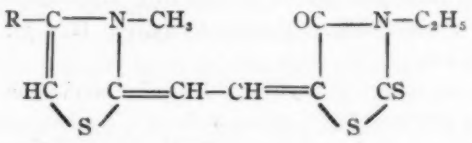


(VIb)



For this system there are two plausible extreme structures which are uncharged and dipolar respectively. The charged structure (VI b) is derived from the uncharged structure (VI a) by transferring an electron from one end of the conjugated system to the other and from nitrogen to oxygen, resulting in rearrangement of double and single bonds.

In the present investigation, merocarbocyanine dyes derived from thiazoles have been described. When $n=1$ in formula VI), the dyes are known as merocyanines. The higher vinylogues of merocyanines (*i.e.*, when $n=1$, 2, or 3) are known respectively as merocarbocyanine, merodicarbocyanine and merotricarbocyanine. Merocarbocyanines (VII) were prepared by treating reactive ketomethylene compound (in the present case 3-ethyl-rhodanine) with intermediates derived from thiazoles and containing the β-anilino- or acetanilidovinyl group.



(VII)

The preparation of thiazoles, their methiodides and the acetanilido intermediates containing conjugated chains are described in the Experimental. The sensitisation spectra and the absorption maxima of these dyes and the variation of deviation with chain length in these series of merocyanine dyes have been studied and will be reported elsewhere.

EXPERIMENTAL

4-p-*Bromophenyl-2-methylthiazole* was prepared by condensing ω-bromo-*p*-bromoacetophenone with thioacetamide (Wetherill and Hann, *J. Amer. Chem. Soc.*, 1934, **56**, 970), m.p. 127°, yield 78%. (Found : C, 47.13 ; H, 3.01. Calc. for $C_{10}H_8NBrS$: C, 47.25 ; H, 3.15%)

4-p-*Bromophenyl-2-methylthiazole methiodide* was prepared by the method of Mills and Smith (*J. Chem. Soc.*, 1922, **121**, 2735) by heating 4-*p*-bromophenyl-2-methylthiazole (2.54 g.) and methyl iodide (1.42 g.) in a sealed tube for 48 hours. The product was washed with cold water and crystallised from ethanol, m. p. 251°, yield 70%. (Found : C, 33.21 ; H, 2.68. $C_{11}H_{11}NBrIS$ requires C, 33.34 ; H, 2.77%).

2-(2-*Acetanilidovinyl*)-4-p-*bromophenylthiazole methiodide* was prepared by heating the preceding methiodide (3.96 g.) and diphenylformamidine (1.96 g.) in acetic anhydride under reflux for an hour. After removal of excess of the solvent, the dark residue was treated with ether, washed with cold water, followed by acetone to remove tarry products. The acetone-washed product was sufficiently pure for further reactions. Pure meterial was obtained by two recrystallisations from acetic acid in orange-brown crystals, m. p. 174-75° (decomp.), yield 56%. (Found : C, 44.21 ; H, 3.25. $C_{20}H_{18}ON_2BrIS$ requires C, 44.36 ; H, 3.33%).

5-[{3-*Methyl* 2-(3H)-4-p-*bromophenylthiazolylidene}-*ethylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—The above methiodide (5.41 g.) and 3-ethyl-rhodanine were refluxed in acetic anhydride in presence of fused sodium acetate for 2 hours. The product after being cooled was washed several times with cold water, followed by acetone, to remove any tarry residue. Pure material was obtained by three recrystallisations from acetic acid in reddish brown plates, m.p. 218-20° (decomp.), yield 48%. (Found : C, 46.39 ; H, 3.37. $C_{17}H_{15}ON_2BrS_3$ requires C, 46.46 ; H, 3.41%).

4-p-*Ethoxyphenyl*-2-*methylthiazole* was prepared by the same method as described in the preceding thiazole by taking *p*-ethoxyphenacyl bromide, m.p. 58°. yield 65%. (Found : C, 65.63 ; H, 5.82. $C_{12}H_{13}ONS$ requires C, 65.77 ; H, 5.93%).

4-p-*Ethoxyphenyl*-2-*methylthiazole Methiodide*.—4-*p* - Ethoxyphenyl-2-methylthiazole (2.19 g.) and methyl iodide (1.42 g.) were heated in a sealed tube for 30 hours. The product was washed with cold water, treated with ether and recrystallised from hot methanol, m.p. 204°, yield 60%. (Found : C, 43.10 ; H. 4.32. $C_{13}H_{16}ONIS$ requires C, 43.21 ; H, 4.43%).

2-(2-*Acetanilidovinyl*)-4-p-*ethoxyphenylthiazole methiodide* was prepared in a similar way as the 4-*p*-bromophenyl analogue from 4-*p*-ethoxyphenyl-2 - methylthiazole methiodide (3.61 g.) and diphenylformamidine (1.96 g.) and purified similarly. Pure material was obtained by two recrystallisations from acetic acid, m.p. 188° (decomp.), yield 48%. (Found : C, 52.05 ; H, 4.41. $C_{22}H_{23}O_2N_2IS$ requires C, 52.17 ; H, 4.54%).

5-[{3-*Methyl*-2(3H)-4-p-*ethoxyphenylthiazolylidene}-*ethylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—A mixture of the preceding methiodide (5.06 g.) and 3-ethyl-rhodanine (1.61 g.)was refluxed in acetic anhydride in presence of fused sodium acetate for 3 hours. After cooling, the product was stirred and washed with cold water, followed by acetone. Pure material was obtained by three recrystallisations from acetic acid from which it separated in deep reddish violet needles, m.p. 167° (decomp.), yield 42%. (Found : C, 56.30 ; H, 4.87. $C_{19}H_{20}O_2N_2S_3$ requires C, 56.43 ; H, 4.95%).

2-*Methylbenzothiazole methiodide* was prepared in the same manner as described in the preceding methiodides and crystallised from hot water, m.p. 217° (*Chem. Abst.*, 1925, **19**, 2339). Doja and Banerjee (this *Journal*, 1946, **23**, 223) report m.p. 219°. The product was obtained in 75% yield (Doja and Banerjee have not recorded the yield of the compound). (Found : C, 37.04 ; H, 3.36. Calc. for $C_9H_{10}NIS$: C, 37.12 ; H, 3.42%).

2-(2-*Acetanilidovinyl*)-*benzothiazole Methiodide*.—The preceding methiodide (2.9 g.) and diphenylformamidine (1.96 g.) in acetic anhydride were heated under reflux for 70 minutes. The product obtained after removing excess of the solvent was treated with ether and washed by acetone. The acetone-washed product was pure enough to be used for further reaction. Pure material was obtained by two recrystallisations from methanol, m.p. 178° (decomp.), yield 58%. (Found : C, 49.43 ; H, 3.75. $C_{18}H_{17}ON_2IS$ requires C, 49.55 ; H, 3.89%).

5-[{3-*Methyl*-2 (3H)-*benzothiazolylidene*}-*ethylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one* was prepared by refluxing the above methiodide (4.36 g.) and 3-ethyl-rhodanine in acetic anhydride in presence of fused sodium acetate for 3 hours. The product,

after being stirred and washed with cold water, was washed with acetone to remove tarry products. Pure material was obtained by three recrystallisations from acetic acid from which it separated as dark red crystals, m.p. 148-49° (decomp.), yield 50%. (Found : C, 53.82 ; H, 4.10. $C_{18}H_{14}ON_2S_3$ requires C, 53.89 ; H, 4.19%).

4-Phenyl-2-methylthiazole and its methiodide, and 4-*p* methoxyphenylthiazole and its methiodide have been prepared and their m.p., yield and analytical data have been reported elsewhere.

2-(2-*Acetanilidovinyl*) - 4 - *phenylthiazole methiodide* was prepared by refluxing 4-phenyl-2-methylthiazole methiodide (3.17 g., 1*M*) and diphenylformamidine (1.96 g., 1*M*) in acetic anhydride (10-15 c.c.) for about an hour. Excess of acetic anhydride was removed by distillation under reduced pressure and the dark residue was treated with ether. The gummy product after being washed with water was solidified by keeping it in contact with methanol and was treated with acetone to remove tarry products. The product was finally recrystallised from hot methanol, m.p. 162-63° (decomp.), yield 55%. (Found : C, 51.89 ; H, 4.04. $C_{20}H_{19}ON_2IS$ requires C, 51.95 ; H, 4.10%).

5-[{3-*Methyl*-2 (3H)-4-*phenylthiazolylidene*}-*ethylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—The above methiodide (4.62 g., 1*M*) and 3-ethyl-rhodanine (1.61 g., 1*M*) were refluxed in acetic anhydride in presence of fused sodium acetate as the condensing agent for 2 hours. After cooling, the material was washed several times with cold water, followed by acetone to remove any tarry residue and was finally recrystallised from hot methanol. Pure material was obtained by two recrystallisations from hot methanol as shining reddish plates, m.p. 176-77° (decomp.), yield 45%. (Found : C, 56.48 ; H, 4.33. $C_{17}H_{16}ON_2S_3$ requires C, 56.66 ; H, 4.44%).

2-(2-*Acetanilidovinyl*)-4 - p - *methoxyphenylthiazole methiodide* was prepared by refluxing 4-*p*-methoxyphenyl-2-methylthiazole methiodide (3.47 g., 1*M*) and diphenylformamidine (1.96 g., 1*M*) in the same way as the corresponding benzothiazole methiodide. Pure material was obtained by two recrystallisations from hot methanol, m.p 178° (decomp.), yield 52%. (Found : C, 51.04 ; H, 4.13. $C_{21}H_{21}O_2N_2IS$ requires C, 51.22 ; H, 4.26%).

5-[{3*Methyl*-2 (3H) 4-p-*methoxyphenylthiazolylidene*}-*ethyiidene*]-3 - *ethyl*-2-*thiothiazolid*-4-*one* was prepared as usual from the preceding thiazole methiodide (4 92 g., 1 *M*) and 3-ethyl-rhodanine (1.61 g., 1*M*) and purified as described before. Pure material was obtained by two recrystallisations from acetic acid in lustrous reddish brown needles, m.p. 173° (decomp.), yield 40%. (Found : C, 55.24 ; H, 4.48. $C_{18}H_{18}O_2N_2S_3$ requires C, 55.39 ; H, 4.61%).

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CATION-EXCHANGE MEASUREMENTS IN THE SOLID PHASE

By A. Chatterjee

Soils are capable of delivering nutrients or metal ions at a much lower moisture status than what is obtained in the pasty condition. Since exchange, if any, in the air-dry state will be very small, it has been studied by using radioactive gold ions, introduced as an exchangeable cation into the clay. The exchange of gold ion has been studied against Na- and Ca-clays by maintaining (*i*) one of the phases in the solid state and (*ii*) both the phases in the solid state. In (*ii*) exchange does take place but to a very small extent, whereas in (*i*) the exchange is quite appreciable.

It has become apparent from the studies of various workers that both cations and anions take part in exchange of soils and clays, and that a considerable amount of these ions can be made available to the growing plants by exchange.

That direct contact of the exchange material and the exchanging ion is not essential for exchange has been demonstrated amongst others by Brown and Albrecht (Res. Bull., No. 477, College of Agric. Mo., 1950) and Chatterjee (*Indian Soc. Soil Sci.*, 1954, **2**, 111). They have shown that the suspension of a cation-saturated clay and a moistened acid resin can exchange their cations even when the two are separated by a cellophane membrane. The isotherm obtained is similar to that usually found in exchange reactions. This may be interpreted by considering exchange of ions present essentially in the double layers of the two systems.

It has been shown by Bradfield (*J. Phys. Chem.*, 1932, **36**, 340) that Na-saturated clays can take up enough Ba^{2+} ions from an aqueous suspension of $BaSO_4$. As the equilibrium between solid $BaSO_4$ and the solution is disturbed, more and more adsorption may take place. Similarly from anorthite Ca^{2+} ions can be exchanged for H^+ ions of the clay (Graham, *Soil Sci.*, 1941, **51**, 65). Kelley (*Proc. 1st. Int. Congr. Soil Sci.*, 1927, **4**, 483) and later on Jenny, Overstreet and others (*Soil Sci.*, 1939, **47**, 257) and Ayers (*ibid.*, 1939, **48**, 9) have shown by means of tracer technique, that the exchange reaction is also possible in the solid phase, appa en ly without the presence of intermediate solution, termed by them as "contact exchange". This phenomenon is based on the assumption that the adsorbed ions are always oscillating, and whenever two exchange spots come closer to each other so that the oscillating zones overlap, both the ions may change their positions, resulting in an exchange.

In order to explore the possibility of exchange in the solid phase, the following experiments have been carried out. Since exchange is likely to be too small to be measured analytically, advantage has been taken of a radioactive tracer. The choice of the particular tracer has been restricted by the question of availability. We have used radioactive gold which has been obtained in a colloidal form.

Experimental

Radioactive gold was at first disolved in aqua regia and the excess of acid and chlorine removed. It was then taken up several times with water and evaporated on

the water-bath. The radioactive gold chloride solution* was then added to the suspensions of Na- and Ca-clays, as a result of which partial exchange occurred. Free electrolytes were then removed by washing and the Au*-clay was dried and part of it made into solid blocks by mixing with polystyrene as a binder resin and hot-moulding in a hydraulic press. Similar blocks were made from Na- and Ca-clays.

The actual experiments consisted in allowing equilibriation to proceed for 3-5 days** between the systems given below.

(1) Na-clay block against Au*-clay block.

(2) Ca-clay block against Au*-clay block.

(3) Na-clay block against Au*-clay suspension.

(4) Ca-clay block against Au*-clay suspension.

(5) Au*-clay block in H-clay suspension.

In the experiments (1) and (2) one block was placed so tightly against the other by means of screw clips that the entire smooth surfaces came in contact with each other. In the experiments (3), (4) and (5), the solid clay blocks were suspended in the clay suspension. After the requisite number of days the blocks were washed thoroughly with water and oven-dried (105°) and the suspensions evaporated and similarly oven-dried. The blocks as well as the dried clays were then subjected to radioactive measurements which consisted of observing the β- counts. The results of these measurements are shown in Table I.

TABLE I

System.	Counting per minutes.
Background	20
1	62 (Na-clay blocks)
2	28 (Ca ,, ,,
3	1120 (Na ,, ,,
4	186 (Ca ,, ,,
5	220 (H-clay suspension)

DISCUSSION

It is clear from the above data that even if the two phases are present in the solid state (Expts. 1 and 2), noticeable amount of exchange takes place, *i.e.*, Au^{*3+} has ex-

* The sample of colloidal gold has been made available through the courtesy of Prof. S. D. Chatterjee of the Jadavpur University, Calcutta, to whom sincere thanks of the author are due. To him and to his co-worker Sri K. G. Banerjee the author is also greatly indebted for the radioactive measurements.

** Since the original radioactive gold solution has already decayed due to storage, the radioactivity of the Au*-clay is still weaker. Consequently, for the sake of expediency, the equilibrium has not been allowed beyond this period, even in the case of both the phases being solid, in which exchange is naturally much slower.

changed position with Na^+ and Ca^{2+}. These two experiments further show that Na^+, as expected, is exchanged to a greater extent than Ca^{2+}. Compared to the solid plase, Au^{*3+} is likely to knock off in suspension a much larger number of Na^+ or Ca^{2+} ions and hence, as experiments (3) and (4) show, the Na-clay and Ca-clay blocks give comparatively high counts. Here also the easy exchangeability of Na^+ in comparison to Ca^{2+} is clearly noticed. Similarly, by keeping the non-radioactive ion in the form of a suspension, as in experiment (5), the same effect is produced, viz., a greater exchange has taken place of H^+ for Au^{*3+} and hence a higher count of the final dried H-Au*-clay.

Sincere thanks of the author are due to Dr. S. K. Mukherjee of the Dept. of Applied Chemistry, Calcutta University, for his helpful guidance and for providing laboratory facilities.

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SHORT NOTES

EFFECT OF AZOTOBACTER ON FIXED NITROGEN

By M. A. Azim and S. D. Saraf

The utilisation of fixed nitrogen by *azotobacter vinelandii* has been investigated by using colorimetric and growth methods. It has been found that butylamine and semicarbazide, which are reduceable to ammonia, are utilised while nitrobenzene, benzyl nitrite and benzyl nitrate, which are not reduceable to ammonia, are not utilised by the bacteria. The lag period in case of compounds utilised increases with increase of concentration. It has been shown in the previous paper (Azim and Saraf, *Biochim. biophys. Acta*, 1956, **21**, 321) that those nitrogenous compounds are utilised by *azotobacter vinelandii* which are likely to be reduced to ammonia. To confirm this further, the utilisation of butylamine, benzylamine, benzyl nitrite and benzyl nitrate, semicarbazide, nitrobenzene and pyridine has been investigated.

Procedure.—The flasks containing identical quantity of sterile medium inoculated with a culture containing 10^9 cells per 25 c.c. were kept at 30° and made 10^{-2}, 10^{-3} or 10^{-4} *M* with respect to the substrate by the addition of a suitable volume of the concentrated substrate solution. A known volume of the test solution was withdrawn at intervals and analysed by the usual colorimetric methods.

Butylamine.—Two concentrations of butylamine were studied (10^{-2} and 10^{-3} *M*). The concentration of the amine was determined colorimetrically in samples withdrawn at intervals with sodium nitroprusside in acetone. The method gave satisfactory results only with higher concentrations of the substrate. It was found that butylamine was utilised after a certain lag period (Table I).

Semicarbazide.—In this case the colorimetric method could not be used due to non-availability of the reagents. Therefore, the growth method (*J. Bact.*, 1950, **60**, 369) was adopted. It was found that semicarbazide was utilised after a certain lag period in concentrations ranging from 10^{-2} to 10^{-6} *M*.

Benzylamine.—Benzylamine was studied in concentration ranging from 10^{-1} to 10^{-3} *M*. It was estimated colorimertically at intervals using sodium nitroprusside in the presence of acetone. It was not utilised by the bacteria inspite of its non-toxic nature.

Benzyl nitrite and benzyl nitrate were studied in concentrations ranging from 10^{-2} to 10^{-4} *M* and estimated colorimetrically—nitrates by phenol disulphonic acid and nitrite by Griess Ilosva's reagent. Like benzylamine they were also not utilised.

In a similar way nitrobenzene and pyridine were studied and none of them were available to azotobacter. The above observations show that the aromatic compounds containing NO_2, NO_3 or NH_2 groups are not utilised by the bacteria even if these groups are present in the side chain.

TABLE I

(Figures represent the percentage of the substrate utilised.)

	Semicarbazide.				Butylamine.		
	10^{-2}.	10^{-3}.	10^{-4}.	10^{-5}.	10^{-6}.	10^{-2}.	10^{-3}.
0 hr.	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0	0 0	0.0
4	0.0	0.0	0.0	0.0	14.3	0.0	0.0
6	0.0	0 0	0.0	11.6	28.6	0.0	0.0
8	0.0	0.0	10.6	23.1	50 0	0 0	0.0
10	0.0	8.0	21.1	34.7	57.2	0.0	10.0
12	6.7	12.0	36.9	46.2	64.3	0.0	20.0
14	13.4	24.0	42.2	57.7	85.8	0.0	30.0
16	20.0	36.0	52.7	69.3	100,0	0.0	45.0
18	24.0	40.0	...	...	...	0.0	...
20	34.3	...	...	100 0	...	5.3	60.0
22	40.0	...	...	...	...	15.8	70.0
24	...	...	94.8	...	...	...	...
26	...	...	100.0	...	...	34.2	90.0
28	...	...	84.0	...	...	42.2	...
29	...	...	...	...	...	...	100 0
30	70.7	88.0	...	...	...	57.9	...
32	73.4	96.0	...	...	...	68.5	...
34	80.0	100.0	...	...	...	84.2	...
36	86 7	...	...	...	...	89.4	...
38	90.7	...	...	...	...	100 0	...
40	100.0	...	...	...	...	...	...

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ON CUPRIC ETHYL ACETOACETATE

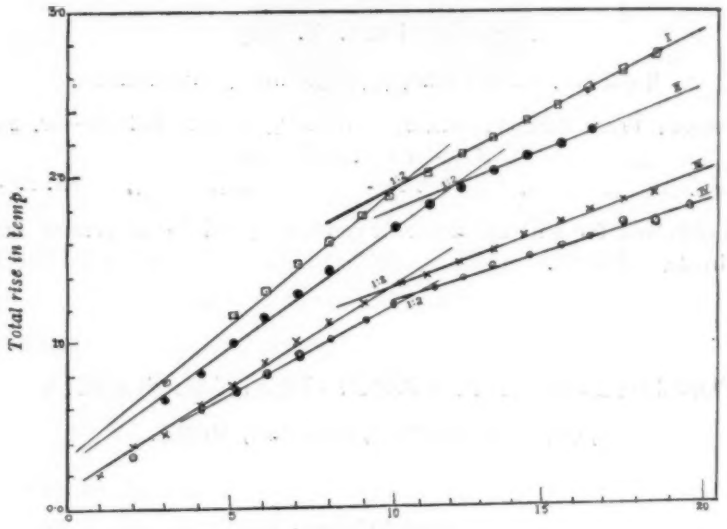
BY G. SITARAMAIAH

The number of neutral chelate oxygen complexes with divalent copper is very large; the ethyl acetoacetate derivative forms cryatals of peculiar green colour, insoluble in water and soluble in common organic solvents (Wislicenus, *Ber.*, 1898, **31**, 3153). Calvin and Wilson studied the stability of this chelate by the p_H titration method (*J. Amer. Chem. Soc.*, 1945, **67**, 2003). During the present investigation the composition of this chelate has been studied by the thermometric titration method of Dutoit (*J. chim. phys.*, 1921, **19**, 324).

The experimental arrangement for the thermometric titration was the same, as used by Halder (this *Journal*, 1946, **23**, 147) and the titrations were done taking all the precautions laid down. The copper salt solution (50 c.c.) was taken in the Dewar flask and titrated with an alcoholic solution of acetoacetic ester. The change in temperature after each addition of the ester was noted with a Beckmann thermometer.

Analar copper sulphate pentahydrate was used to prepare the solutions ; the solutions had a strength of $M/8$ with respect to sodium acetate, which was used to raise the p_H of the solutions. The ester solutions were all made in 50% alcohol (v/v).

FIG. 1



I 0.05569 *M* Cu^{2+} with 0.5432 *M* ester
II 0.03656 *M* ,, ,, 0.3103 *M* ,,
III 0.02352 *M* ,, ,, 0.2483 *M* ,,
IV 0.01919 *M* ,, ,, 0.1901 *M* ,,

In Fig. 1, the total change of temperature was plotted against the volume of ester added. All the curves show that the complex cupric ethyl acetoacetate formed during the titrations has the compositon, $Cu(C_6H_9O_3)_2$. Thus, the thermometric study corroborates the conclusion drawn about the composition of this complex, by other methods.

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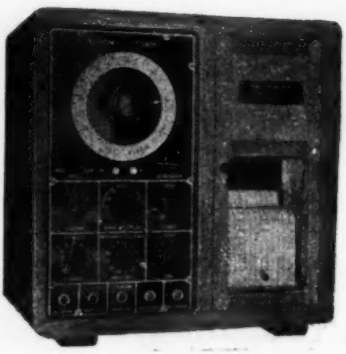

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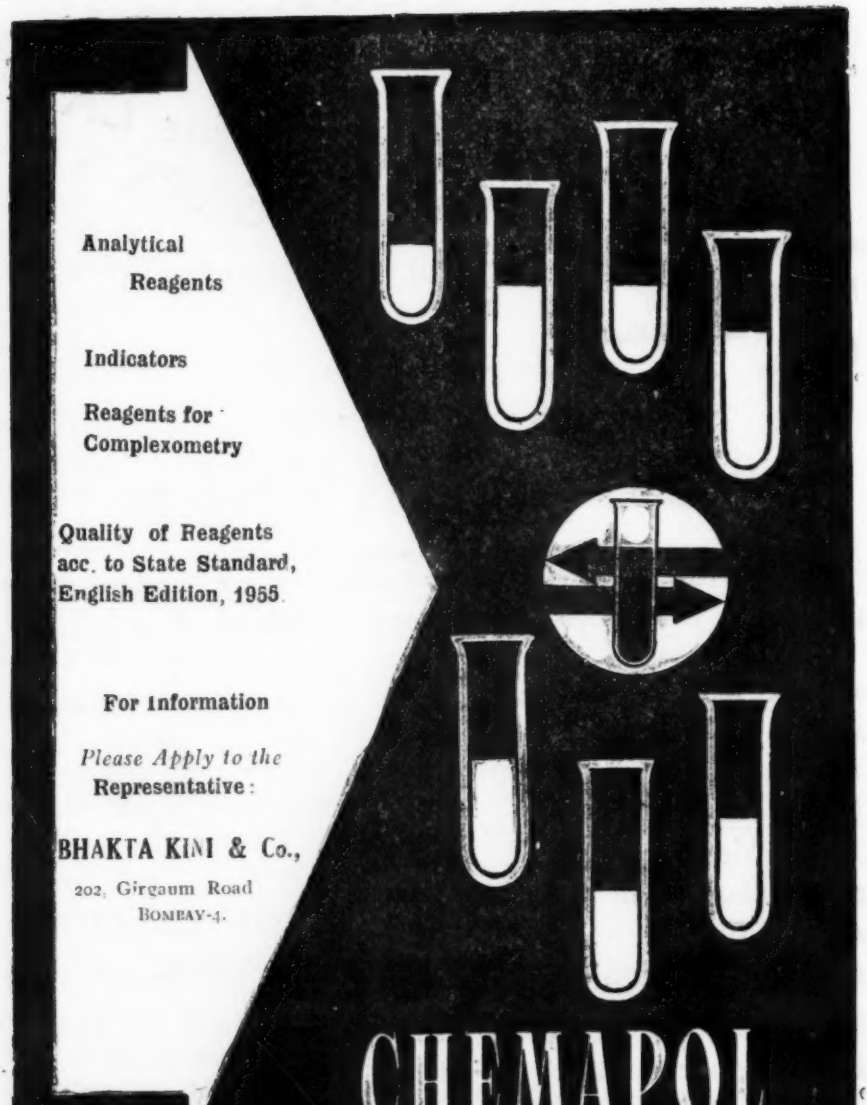

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